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Selected Processes

IT Enviroscience
Knoxville, TN

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EPA is developing new source performance standards under Section 111 of the Clean Air Act and national emission standards for hazardous air pollutants under Section 112 for volatile organic compound emissions (VOC) from organic chemical manufacturing facilities. In support of this effort, data were gathered on chemical processing routes, VOC emissions, control techniques, control costs, and environmental impacts resulting from control. These data have been analyzed and assimilated into the ten volumes comprising this report.

This volume presents in-depth studies of several major organic chemical products.

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Organic Chemical Manufacturing
Volume 10: Selected Processes

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
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02

December 1980

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INTRODUCTION

A. SOCMI PROGRAM

Concern over widespread violation of the national ambient air quality standard for ozone (formerly photochemical oxidants) and over the presence of a number of toxic and potentially toxic chemicals in the atmosphere led the Environmental Protection Agency to initiate standards development programs for the control of volatile organic compound (VOC) emissions. The program goals were to reduce emissions through three mechanisms: (1) publication of Control Techniques Guidelines to be used by state and local air pollution control agencies in developing and revising regulations for existing sources; (2) promulgation of New Source Performance Standards according to Section 111(b) of the Clean Air Act; and (3) promulgation, as appropriate, of National Emission Standards for Hazardous Air Pollutants under Section 112 of the Clean Air Act. Most of the effort was to center on the development of New Source Performance Standards.

One program in particular focused on the synthetic organic chemical manufacturing industry (SOCMI), that is, the industry consisting of those facilities primarily producing basic and intermediate organics from petroleum feedstock meterials. The potentially broad program scope was reduced by concentrating on the production of the nearly 400 higher volume, higher volatility chemicals estimated to account for a great majority of overall industry emissions. EPA anticipated developing generic regulations, applicable across chemical and process lines, since it would be practically impossible to develop separate regulations for 400 chemicals within a reasonable time frame.

To handle the considerable task of gathering, assembling, and analyzing data to support standards for this diverse and complex industry, EPA solicited the technical assistance of IT Enviroscience, Inc., of Knoxville, Tennessee (EPA Contract No. 68-02-2577). IT Enviroscience was asked to investigate emissions and emission controls for a wide range of important organic chemicals. Their efforts focused on the four major chemical plant emission areas: process vents, storage tanks, fugitive sources, and secondary sources (i.e., liquid, solid, and aqueous waste treatment facilities that can emit VOC).

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B. REPORTS

To develop reasonable support for regulations, IT Enviroscience gathered data on about 150 major chemicals and studied in-depth the manufacture of about 40 chemical products and product families. These chemicals were chosen considering their total VOC emissions from production, the potential toxicity of emissions, and to encompass the significant unit processes and operations used by the industry. From the in-depth studies and related investigations, IT Enviroscience prepared 53 individual reports that were assembled into 10 volumes. These ten volumes are listed below:

Volume 1 : Study Summary
Volume 2 : Process Sources
Volume 3 : Storage, Fugitive, and Secondary Sources
Volume 4 : Combustion Control Devices
Volume 5 : Adsorption, Condensation, and Absorption Devices
Volume 6-10: Selected Processes

This volume is a compilation of individual reports for the following chemical products: propylene oxide, acrylonitrile, glycerin and its intermediates, acrylic acid and esters, methyl methacrylate, chloroprene, butadiene, acetic anhydride, acetic acid, formic acid, ethyl acetate, methyl ethyl ketone, and sulfuric acid. The reports generally describe processes used to make the products, VOC emissions from the processes, available emission controls, and the costs and impacts of those controls (except that abbreviated reports do not contain control costs and impacts). Information is included on all four emission areas; however, the emphasis is on process vents. Storage tanks, fugitive sources, and secondary sources are covered in greater detail in Volume III. The focus of the reports is on control of new sources rather than on existing sources in keeping with the main program objective of developing new source performance standards for the industry. The reports do not outline regulations and are not intended for that purpose, but they do provide a data base for regulation development by EPA.

C. MODEL PLANTS

To facilitate emission control analyses, the reports introduce the concept of a "model plant" (not in abbreviated reports). A model plant by definition is a representation of a typical modern process for production of a particular chemical. Because of multiple production routes or wide ranges in typical production

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capacities, several model plants may be presented in one product report. The model plants can be used to predict emission characteristics of a new plant. Of course, describing exactly what a new plant will be like is difficult because variations of established production routes are often practiced by individual companies. Nonetheless, model plants provide bases for making new-plant emission estimates (uncontrolled and controlled), for selecting and sizing controls for new plants, and for estimating cost and environmental impacts. It is stressed that model-plant analyses are geared to new plants and therefore do not necessarily reflect existing plant situations.

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REPORT 1

PROPYLENE OXIDE

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Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

December 1980

This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	$1\ Tg = 1 \times 10^{12}$ grams
G	giga	10^{9}	$1\ Gg = 1 \times 10^{9}$ grams
M	mega	10^{6}	$1\ Mg = 1 \times 10^{6}$ grams
k	kilo	10^{3}	$1\ km = 1 \times 10^{3}$ meters
m	milli	10^{-3}	$1\ mV = 1 \times 10^{-3}$ volt
μ	micro	10^{-6}	$1\ \mu g = 1 \times 10^{-6}$ gram

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II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Propylene oxide production was selected for study because preliminary estimates indicated that production of this material generated a fairly large amount of air emissions. In addition, the manufacture of propylene oxide is a large and growing industry.[1]

Many of the raw materials, intermediates, finished products, by-products, and organic waste streams handled or generated in the manufacture of propylene oxide have relatively high vapor pressure (low boiling points); so vents and other emission sources are likely to discharge significant amounts of organic vapors to the air unless appropriate emission control techniques are used.

B. PROPYLENE OXIDE USAGE AND GROWTH[1,2]

Table II-1 shows propylene oxide production and growth rates. The predominant use of propylene oxide is in the manufacture of polyether polyols used for the manufacture of urethane foams. Use of propylene oxide for manufacture of polyether polyols has varied from 52% to 62% of the total propylene oxide consumed domestically in the period 1974 to 1978. The other principal uses for propylene oxide are in the manufacture of propylene glycol (21 to 23%), dipropylene glycol (2.5 to 2.9%), and glycol ethers (1.2 to 1.5%). Miscellaneous uses accounted for the balance of the propylene oxide consumed.

Some propylene oxide is sold on the open market to processors that convert it to other intermediates or finished products, but a large share of the total amount manufactured is used by the producers to make other intermediates or finished products. Because of this large internal consumption by integrated producers, the production data shown in Table II-1 are expected to contain some inaccuracies, but they represent the best numbers available. The current projected growth of 5.3 to 7.1% per year is expected to continue through 1982.

C. DOMESTIC PRODUCERS

As of January 1979 four producers of propylene oxide in the United States were operating plants at six locations. Table II-2 lists the producers, plant capacity, and type of process used in the plant. Figure II-1 shows the location of the six domestic plants.[1]

Table II-1. Propylene Oxide Production and Growth*

Year	Production Rate (Gg/yr)	Growth Rate (%/yr)
1958	73	25.2
1959	131	
1960	140	
1961	170	
1962	202	
1963	225	
1964	258	14.0
1965	274	
1966	322	
1967	369	
1968	434	
1969	534	12.9
1970	535	
1971	542	
1972	689	
1973	795	
1974	797	3.1
1975	691	
1976	827	
1977	846	
1978	927	
1982 (est)	1116—1215	5.3—7.1

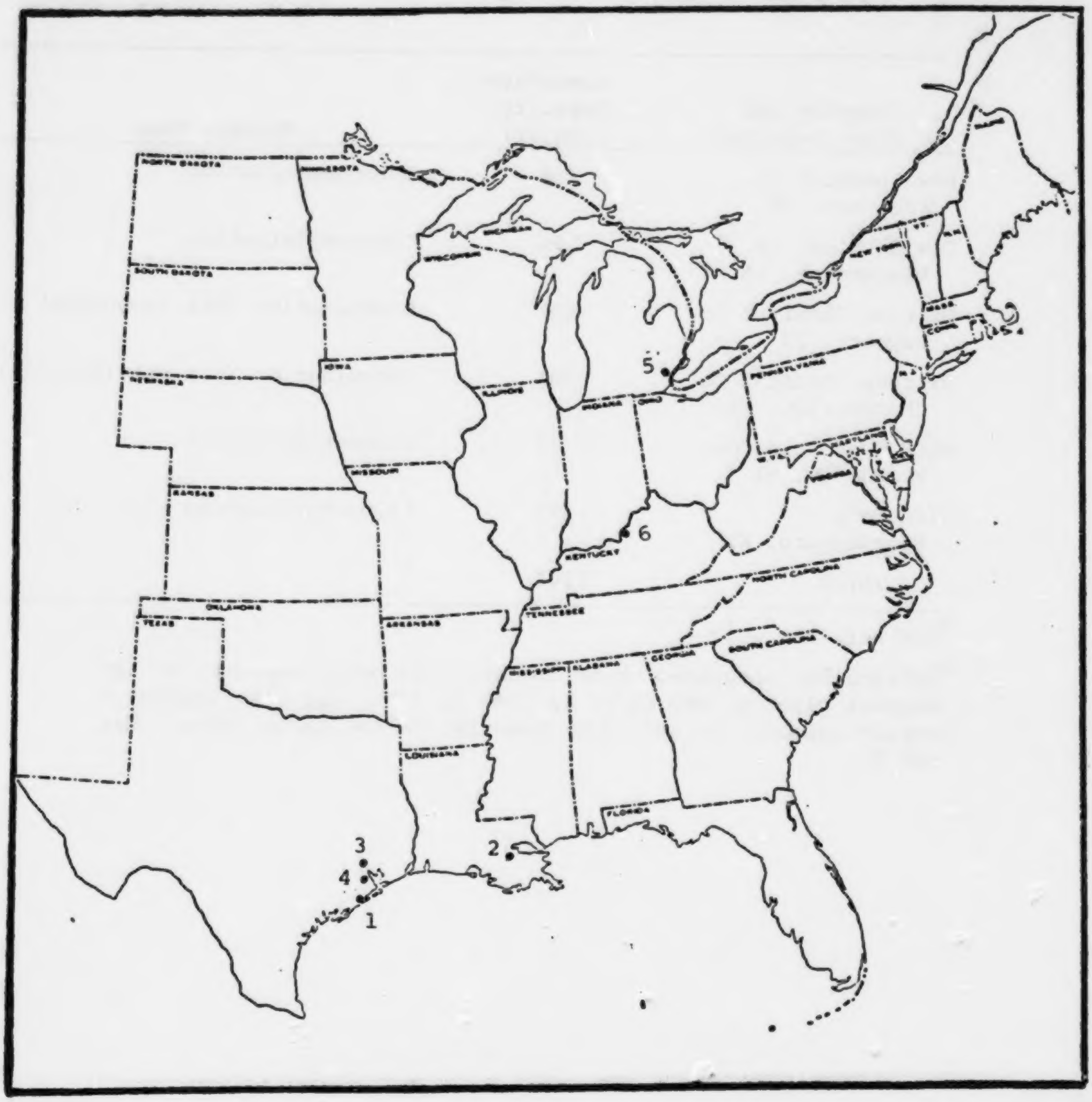
*See refs 1 and 2.

Table II-2. Propylene Oxide Production Capacity, January 1979[a]

Company and Plant Location	Nameplate Capacity (Gg/yr)	Process Type
Dow Chemical Co. Freeport, TX	454	Chlorohydrination
Dow Chemical Co. Plaquemine, LA	154	Chlorohydrination
Oxirane Chemical Co. Bayport, TX	417[b]	Peroxidation (via isobutane)
Oxirane Chemical Co. Channelview, TX	181	Peroxidation (via ethylbenzene)
BASF Wyandotte Corp. Wyandotte, MI	79	Chlorohydrination
Olin Corp. Brandenburg, KY	59	Chlorohydrination
Total	1344	

[a] See ref 1.

[b] Oxirane has announced their intention to boost capacity of the Bayport plant to 463 Gg/yr in 1980 or 1981, and also intends to expand capacity to 644 Gg/yr sometime in the early 1980s. See ref 3.



1. The Dow Chemical Co., Freeport, TX
2. The Dow Chemical Co., Plaquemine, LA
3. Oxirane Corp., Channelview, TX
4. Oxirane Corp., Bayport, TX
5. BASF Wyandotte Corp., Wyandotte, MI
6. Olin Corp., Brandenburg, KY

17 Fig. II-1. Locations of Plants Manufacturing Propylene Oxide

Jefferson Chemical Co. (Texaco, Inc.) shut down their plant at Port Neches, TX, in December 1978.[3]

The rated capacity for domestic plants manufacturing propylene oxide was 1344 Gg/yr in January 1979. The current capacity is reported to be 1435 Gg/yr. With the announced expansions by Oxirane at their Bayport plant, the total production capacity is expected to reach 1480 Gg/yr in 1980 or 1981 and to rise further to 1662 Gg/yr in the early 1980s.[1—3]

Reported domestic production for propylene oxide was 927 Gg in 1978, which is only 69% of the 1979 production capacity. Production in 1982 is estimated to be in the range of 1116 to 1215 Gg/yr, which amounts to only 75 to 82% of the announced 1981 production capacity.[2,3]

With production rates running well below present and announced capacity, it is considered likely that other older, less efficient, chlorohydrination process plants will be shut down in the near future. If the two remaining small producers (Olin and BASF Wyandotte) decide to shut down, the remaining producers will be Dow Chemical Co. and Oxirane Chemical Co., both giants in the field of propylene oxide manufacture.

D. REFERENCES*

1. S. A. Cogswell, "Propylene Oxide," pp. 690.8021A—690.8023D in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (July 1979).

2. S. L. Soder and K. L. Ring with R. E. Davenport, "Propylene," pp. 300.5403J, K, U, V, W, X in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (August 1978).

3. "Chementator," Chemical Engineering, p. 83 (Apr. 23, 1979).

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

III. PROCESS DESCRIPTIONS

A. INTRODUCTION

In the United States at present all propylene oxide is manufactured from purified propylene.[1] The two commercial processes currently practiced are the older chlorohydrination route using chlorine and caustic (or other alkali) and the newer hydroperoxide route in which a relatively easily oxidized hydrocarbon, such as isobutane or ethylbenzene, is oxidized to the corresponding hydroperoxide by air or purified oxygen. The hydroperoxide in turn is used to epoxidize propylene to propylene oxide. The by-product alcohol from the epoxidation step is either purified and sold as a coproduct or further processed to a useful coproduct.[1—4]

The reactions involved in oxidizing propylene to propylene oxide are exothermic and produce significant quantities of heat. Because of the temperatures and reaction conditions at which this heat is released, it is difficult to convert this exothermic heat energy to useful forms of energy, such as steam, and most of the heat is rejected to the environment.[2—4]

B. CHLOROHYDRINATION PROCESS[1—5]

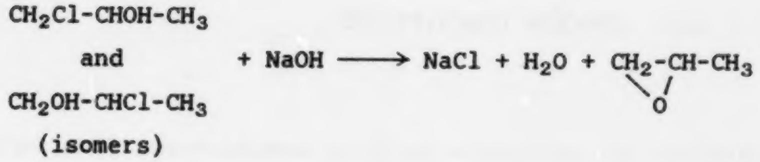
1. General Discussion

This process route uses a two-step reaction sequence in which chlorine is first used in an aqueous solution to chlorohydrinate propylene to propylene chlorohydrin. A simplified overall equation for this first reaction is as follows:

$$Cl_2 + H_2O + CH_2{=}CH\text{-}CH_3 \longrightarrow HCl + \begin{array}{c} CH_2Cl\text{-}CHOH\text{-}CH_3 \\ \text{and} \\ CH_2OH\text{-}CHCl\text{-}CH_3 \\ \text{(isomers)} \end{array}$$

Conditions that promote high yields and minimum amounts of by-products are low pH, dilute solution, and relatively low reaction temperature.

The second reaction step is the reaction of the chlorohydrin isomers with an alkali [usually NaOH or $Ca(OH)_2$] to convert the chlorohydrins to propylene oxide. A simplified overall equation for this second reaction is as follows:



$$\begin{array}{c} CH_2Cl\text{-}CHOH\text{-}CH_3 \\ \text{and} \\ CH_2OH\text{-}CHCl\text{-}CH_3 \\ \text{(isomers)} \end{array} + NaOH \longrightarrow NaCl + H_2O + \underset{\diagdown O \diagup}{CH_2\text{-}CH\text{-}CH_3}$$

This reaction takes place at elevated temperature under slight pressure. Reaction conditions are selected so that the propylene oxide is vaporized as it is generated, and the propylene oxide is then condensed as a crude product stream to separate the oxide from the large wastewater stream containing salt and traces of organic waste material.

The principal by-products generated in this two-step reaction sequence are dichloropropane (DCP) and dichloroisopropyl ether (DCIPE). Other miscellaneous organic compounds are generated in minor quantities. These miscellaneous materials are separated during the product purification steps and are discarded as waste streams.

Industry data indicate that with the chlorohydrin process about 0.9 g of propylene is consumed per gram of propylene oxide produced.[1,5]

The chlorohydrin process is the older process route for the manufacture of propylene oxide and consumes large quantities of chlorine and caustic (or other alkali). Since both chlorine and alkali require large amounts of energy to manufacture, the current pressure of high and rising prices for energy make it unlikely that this process route will be the route selected when new manufacturing plants are constructed.

In the recent past old production plants previously used for the manufacture of ethylene oxide by the chlorohydrin route have been converted to manufacture of propylene oxide by this same reaction mechanism. These plants became available when the production of ethylene oxide was switched to new, direct oxidation plants in which air or oxygen was used to convert ethylene to ethylene oxide. Since almost all the old plants have now either been converted for manufacture of propylene oxide or shut down and dismantled, this route for expansion of propylene oxide capacity is no longer readily available. Some capacity expansion could still be made by modifying or debottlenecking these older chlorohydrination plants, but it is very unlikely that new plants will be built for the old chlorohydrination process.

2. Process Technology

Figure III-1 is a copy of the block flowsheet furnished by The Dow Chemical Company for the chlorohyrination route to propylene oxide.[6] The model plant* flowsheet for the chlorohydrination process for propylene oxide given in Fig. III-2, pp. 1 and 2, is based on the Dow flowsheet, on the process description given in the nonconfidential trip report,[6] on the process descriptions given in the three SRI Process Economics Program Reports,[2—4] and on physical property data. The process shown probably is not an exact representation of the chlorohydrination process as practiced by any of the manufacturers of propylene oxide by this route but is believed to be sufficiently representative to be useful for air emission purposes.

In the process shown on Fig. III-2 chlorine vapor (1) is mixed into and reacts with chilled process water (3) to form hydrochloric acid and hypochlorous acid. This large aqueous stream (4) of dilute hypochlorous acid then contacts propylene vapor (2 + 5) in chlorohydrination reactors, where the propylene is converted to the two isomeric forms of propylene chlorohydrin dissolved in water (8). The unreacted propylene (5) is recycled to the chlorohydrin reactors, while a bleed stream (6) of propylene containing residual propane and other inert gases is fed to a vent gas scrubber. Dilute caustic (7) is used as the absorption fluid in the vent gas scrubber to absorb and remove any traces of hydrochloric acid vapor or chlorine gas from the vent gas stream (A_1). The wastewater (K_1) from the scrubber is discharged to the plant wastewater system.

The dilute chlorohydrin solution (8) is mixed with an alkali solution (9) or slurry, and fed to a saponification column, where the alkali reacts with the propylene chlorohydrin to form salt and propylene oxide. Temperature and pressure inside the saponification column are controlled so that the propylene oxide is vaporized and stripped out of the aqueous reaction mixture. The wastewater from the saponifier (K_2) contains salt and some residual organic materials. This wastewater stream (K_2) is discharged to the plant wastewater system. The vent gas stream from the saponifier column is labeled A_2.

The crude propylene oxide from the saponifier is condensed (10) and fed to the propylene oxide stripping column. This stripping column separates the propylene oxide and other low-boiling components from the higher boiling chlorinated

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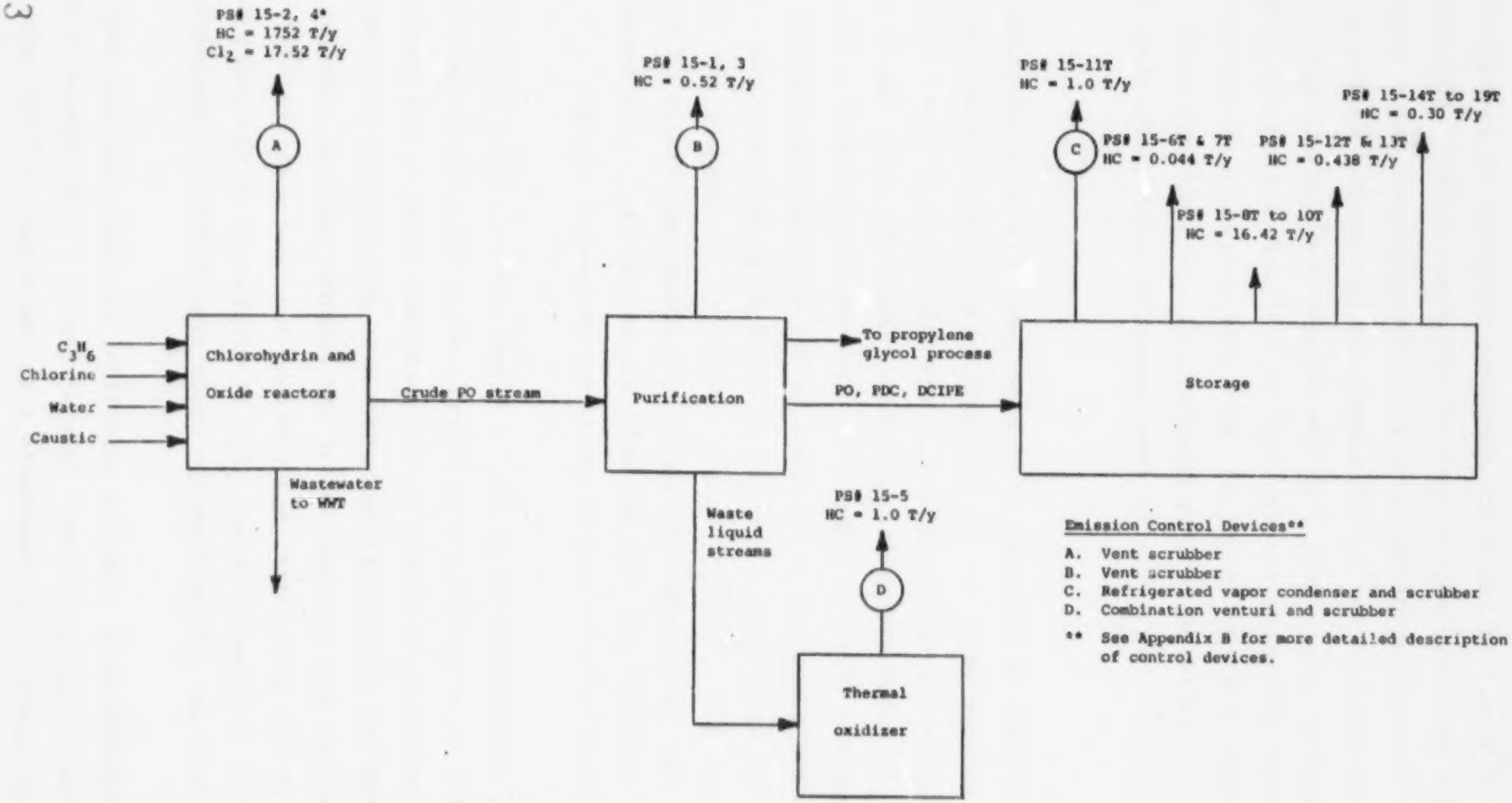
*See p I-2 for a discussion of model plants.


PS# 15-2, 4*
HC = 1752 T/y
Cl_2 = 17.52 T/y
A
C_3H_6
Chlorine
Water
Caustic
Chlorohydrin and
Oxide reactors
Wastewater to WWT
Crude PO stream
PS# 15-1, 3
HC = 0.52 T/y
B
Purification
To propylene glycol process
PO, PDC, DCIPE
Waste liquid streams
PS# 15-5
HC = 1.0 T/y
D
Thermal oxidizer
PS# 15-11T
HC = 1.0 T/y
C
PS# 15-6T & 7T
HC = 0.044 T/y
PS# 15-8T to 10T
HC = 16.42 T/y
PS# 15-12T & 13T
HC = 0.438 T/y
PS# 15-14T to 19T
HC = 0.30 T/y
Storage

Emission Control Devices**

A. Vent scrubber
B. Vent scrubber
C. Refrigerated vapor condenser and scrubber
D. Combination venturi and scrubber

** See Appendix B for more detailed description of control devices.

*See Appendix A for point source (PS) emission data as reported on Louisiana Emission Inventory Questionnaire.

Fig. III-1. Dow/Plaquemine Propylene Oxide Flow Diagram

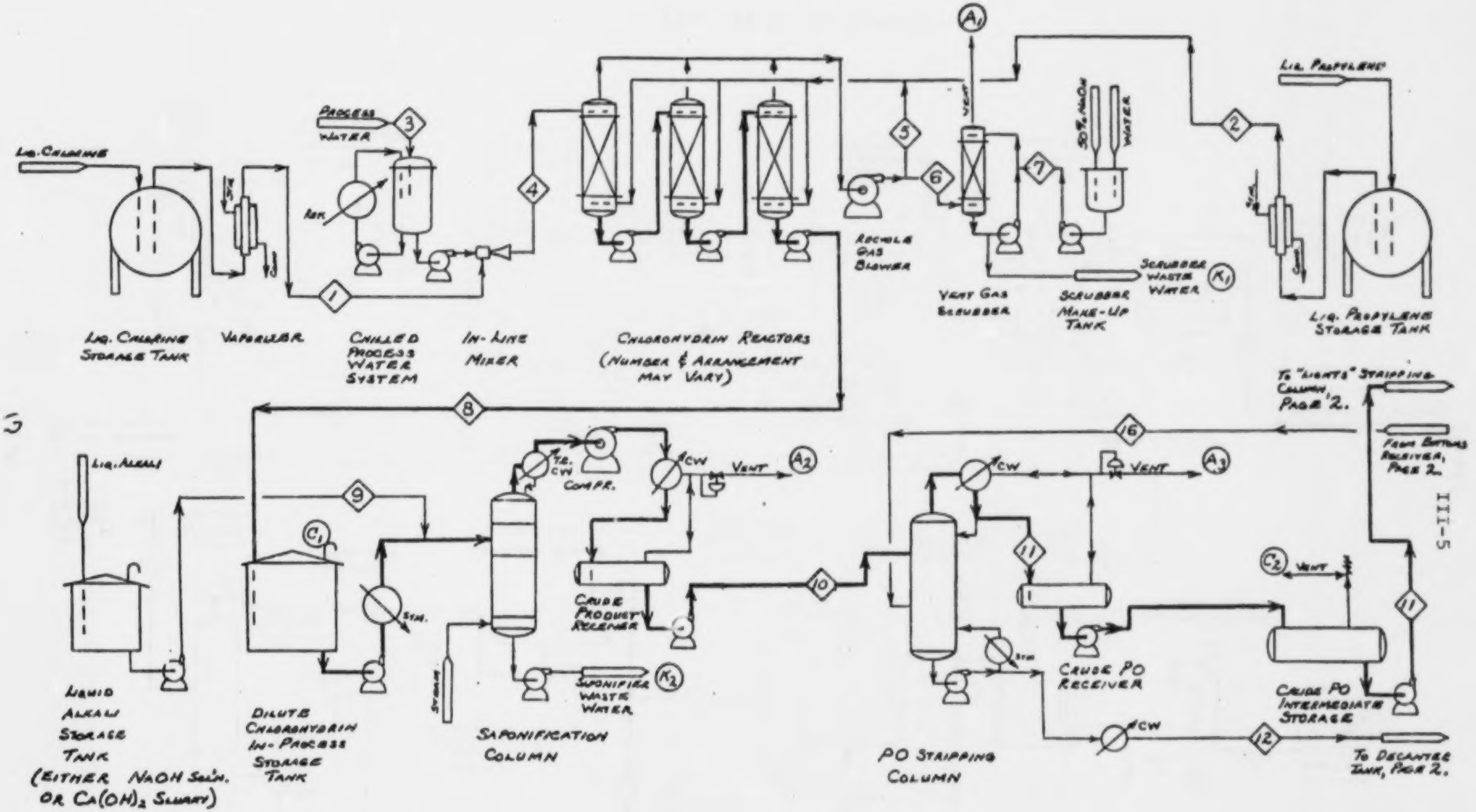

LIQ. CHLORINE
LIQ. CHLORINE STORAGE TANK
STM.
VAPORIZER
PROCESS WATER
3
REFR.
CHILLED PROCESS WATER SYSTEM
1
IN-LINE MIXER
4
CHLOROHYDRIN REACTORS (NUMBER & ARRANGEMENT MAY VARY)
RECYCLE GAS BLOWER
5
6
A1
VENT
VENT GAS SCRUBBER
7
50% NaOH
WATER
SCRUBBER MAKE-UP TANK
SCRUBBER WASTE WATER
K1
2
STM.
LIQ. PROPYLENE
LIQ. PROPYLENE STORAGE TANK
8
LIQ. ALKALI
LIQUID ALKALI STORAGE TANK (EITHER NaOH SOL'N. OR Ca(OH)2 SLURRY)
9
C1
DILUTE CHLOROHYDRIN IN-PROCESS STORAGE TANK
STM.
STEAM
SAPONIFICATION COLUMN
T.R. CW
COMPR.
CW
VENT
A2
CRUDE PRODUCT RECEIVER
SAPONIFIER WASTE WATER
K2
10
16
CW
VENT
A3
11
PO STRIPPING COLUMN
STM
CRUDE PO RECEIVER
CW
12
C2
VENT
CRUDE PO INTERMEDIATE STORAGE
11
TO "LIGHTS" STRIPPING COLUMN, PAGE 2.
FROM BOTTOMS RECEIVER, PAGE 2.
TO DECANTER TANK, PAGE 2.

Fig. III-2. Flow Diagram for Model Plant (Uncontrolled) for PO by Chlorohydrination

(page 1 of 2)

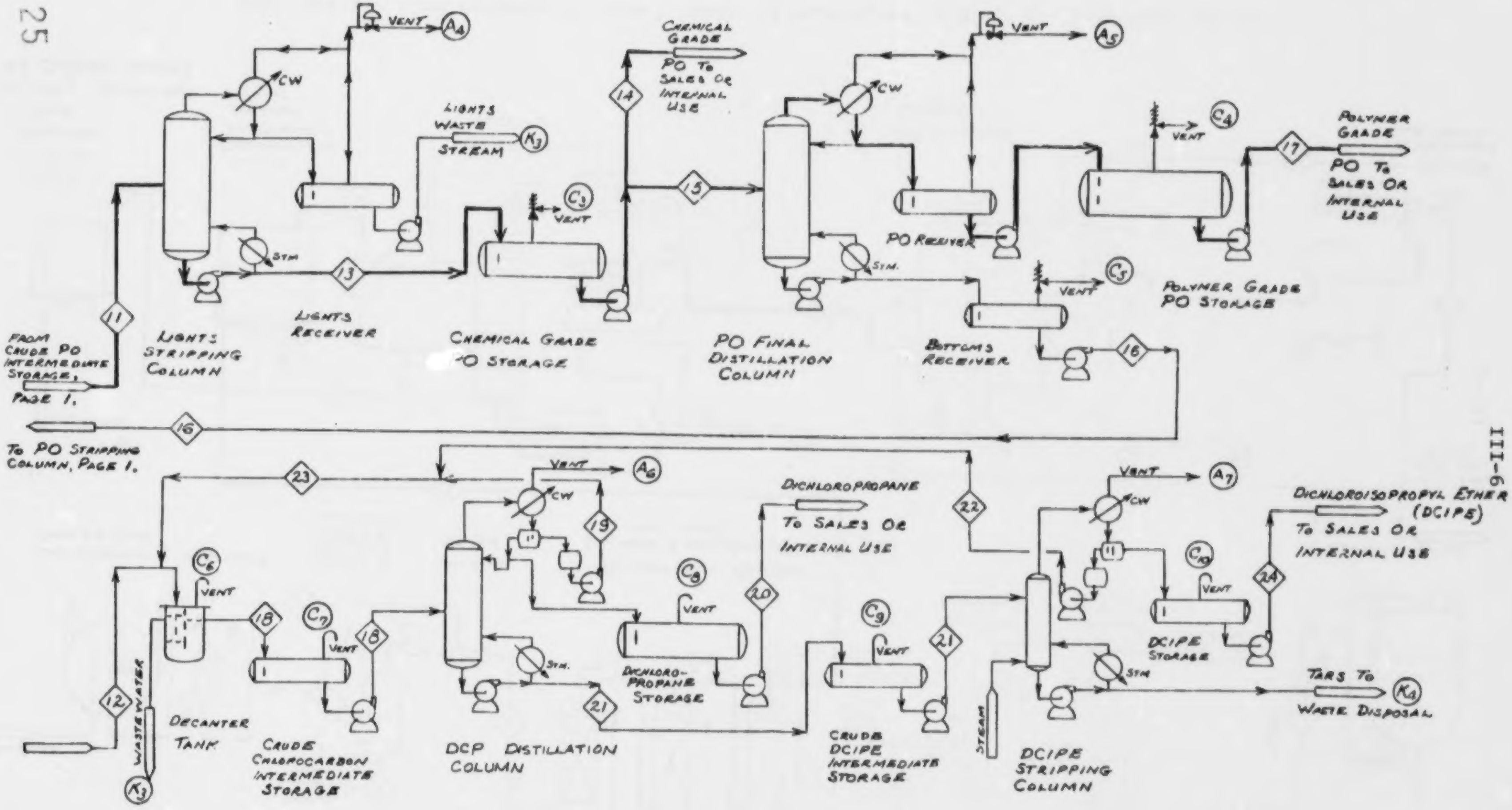

VENT
A4
CW
LIGHTS WASTE STREAM
K3
FROM CRUDE PO INTERMEDIATE STORAGE, PAGE 1.
11
LIGHTS STRIPPING COLUMN
STM
13
LIGHTS RECEIVER
C3
VENT
CHEMICAL GRADE PO STORAGE
14
CHEMICAL GRADE
PO TO SALES OR INTERNAL USE
15
PO FINAL DISTILLATION COLUMN
CW
VENT
A5
STM.
PO RECEIVER
C5
VENT
BOTTOMS RECEIVER
16
C4
VENT
POLYMER GRADE PO STORAGE
17
POLYMER GRADE
PO TO SALES OR INTERNAL USE
16
TO PO STRIPPING COLUMN, PAGE 1.
23
VENT
A6
CW
19
C6
VENT
18
C7
VENT
18
12
WASTEWATER
K3
DECANTER TANK
CRUDE CHLOROCARBON INTERMEDIATE STORAGE
DCP DISTILLATION COLUMN
STM.
21
C8
VENT
DICHLORO-PROPANE STORAGE
20
DICHLOROPROPANE
TO SALES OR INTERNAL USE
C9
VENT
CRUDE DCIPE INTERMEDIATE STORAGE
21
22
VENT
A7
CW
STEAM
DCIPE STRIPPING COLUMN
STM
C10
VENT
DCIPE STORAGE
24
DICHLOROISOPROPYL ETHER (DCIPE)
TO SALES OR INTERNAL USE
TARS TO WASTE DISPOSAL
K4

Fig. III-2. (Continued)

(page 2 of 2)

organic by-products. The vent gas stream from this column is labeled A_3. The overhead stream (11) from this column is fed to the lights stripping columns for separation of the low-boiling impurities (K_3) from the main product stream (13). The vent gas stream from the lights stripping column is labeled A_4.

The main-product stream (13) from the bottom of the lights stripping column may be sold or used (14) for manufacture of other products, or it may be refined further by being sent (15) to a final distillation column, where high-purity product (17) is separated from residual trace impurities (16). The vent gas stream from this final distillation column is labeled A_5.

The bottoms stream (16) from the final distillation column is returned to the propylene oxide stripping column for recovery of residual propylene oxide.

The bottoms stream (12) from the propylene oxide stripping column is sent to a decanter for removal of residual water (K_3), which is sent to the plant wastewater treatment system. The organic layer (18) from the decanter is sent to the DCP distillation column, where dichloropropane (20) is separated from the by-product stream. Any residual water that goes overhead (19) with the dichloropropane (DCP) is separated and recycled to the decanter tank. The vent gas stream from the DCP distillation column is labeled A_6.

The bottoms stream (21) from the DCP distillation column is fed to the DCIPE stripping column, where dichloroisopropyl ether is distilled overhead to yield a stream (24) of purified dichloroisopropyl ether for sale or for internal plant use. The bottoms stream (K_4) from this still is sent to waste disposal. The vent gas stream from this stripping column is labeled A_7.

3. Process Variations

The C. E. Lummus firm has developed a variation of the chlorohydrin process in which the chlorohydrination and saponification reactions are integrated with electrolytic generation of chlorine and caustic from brine by use of t-butyl alcohol converted to t-butyl hypochlorite. The brine resulting from the saponification reaction is recycled to the electrolytic cells for regeneration of the chlorine and caustic consumed in the chlorohydrination and saponification steps. Lummus is offering process licenses and/or construction of production plants by this process. A demonstration plant of unspecified capacity is being built at Bloomfield, NJ.[7]

Other variations of the electrolytic chlorohydrin process for production of propylene oxide are discussed in SRI reports, but commercial plants using these techniques have not been built in the United States.[3,4]

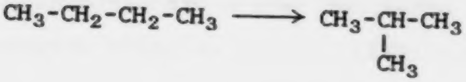
C. HYDROPEROXIDE PROCESSES[1—5]

1. General Discussion

Two versions of the hydroperoxide process for the manufacture of propylene oxide are practiced domestically by the Oxirane Corporation. Oxirane at Bayport, TX, uses isobutane to form t-butyl hydroperoxide for epoxidation of propylene to propylene oxide. The coproduct formed by using isobutane to make hydroperoxide is t-butyl alcohol. Oxirane at Channelview, TX, uses ethylbenzene to form ethylbenzene hydroperoxide for expoxidation of propylene to propylene oxide. The coproduct formed by using ethylbenzene as the hydroperoxide is α-methyl benzyl alcohol. This alcohol, in turn, is converted to styrene monomer by a dehydration reaction, and the resultant styrene coproduct is purified and sold.[1,5]

2. Isobutane Hydroperoxidation Process

a. Process Chemistry——In an adjacent refinery, isobutane is produced from a mixed stream of butane isomers. The mixed butane isomer stream is purified and isomerized to convert the n-butane in the mixed stream to isobutane. This conversion is represented by a simplified equation as follows:



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_3$$

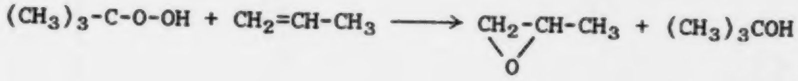
In the hydroperoxide process the isobutane feedstock is oxidized to t-butyl hydroperoxide in a liquid-phase oxidation process. Some of the isobutane is oxidized to t-butyl alcohol in this oxidation step. This oxidation process is represented by two simplified equations:

$$(CH_3)_3CH + O_2 \longrightarrow (CH_3)_3C\text{-}O\text{-}OH$$

$$2(CH_3)_3CH + O_2 \longrightarrow 2(CH_3)_3COH$$

Depending on reaction conditions the yields of hydroperoxide and alcohol can be shifted, but normal yields of hydroperoxide and alcohol are about equal.

The next step in the reaction sequence is the epoxidation of propylene with *t*-butyl hydroperoxide to yield propylene oxide and *t*-butyl alcohol. A catalyst is used to promote this epoxidation reaction. The following simplified equation represents this epoxidation step:



$$(CH_3)_3\text{-C-O-OH} + CH_2\text{=CH-CH}_3 \longrightarrow \underset{\diagdown\ O\ \diagup}{CH_2\text{-CH-CH}_3} + (CH_3)_3COH$$

Separation and purification of the products after this reaction sequence yield commercially pure grades of propylene oxide and *t*-butyl alcohol.

Impurities generated in the process include carbonyl compounds, glycols, ethers, and other miscellaneous organic materials and tars. These impurities must be removed from the product streams and treated by suitable waste disposal techniques.

b. *Process Technology*—Figure III-3 is a copy of the block flowsheet for the Oxirane, Bayport, propylene oxide—*t*-butyl alcohol process as furnished by the Oxirane Corp.[8] Oxirane also includes manufacture of propylene glycol, dipropylene glycol, and isobutylene within the boundary limits of this manufacturing facility.[9] Based on this flowsheet and the accompanying nonconfidential listing of emissions, waste discharges, and control devices given in the Oxirane letter,[8] as well as on the process descriptions given in the three SRI Process Economics Program Reports,[2—4] and on physical property data, a model-plant flowsheet has been constructed for this process. The flowsheet is shown in Fig. III-4, pp. 1—4. The process shown probably is not an exact representation of the peroxidation process as practiced by Oxirane at their Bayport plant, but is believed to be sufficiently representative to be useful for air emission purposes.

In this process liquid isobutane (1 and 8), along with oxygen gas (2), is fed as separate streams into oxidation reactors, where the isobutane is oxidized to *t*-butylhydroperoxide and *t*-butyl alcohol (TBA). Residual (inert) gas and volatile organic compounds (VOC) from the reactors (3) pass through a caustic scrubber, where carbonyl compounds are stripped from the gas. After caustic scrubbing, the gas stream (4) passes through a TBA scrubber, where chilled *t*-butyl alcohol is used to absorb organic vapors from the gas stream. After scrubbing, the vent gases are discharged as vent stream A_1.

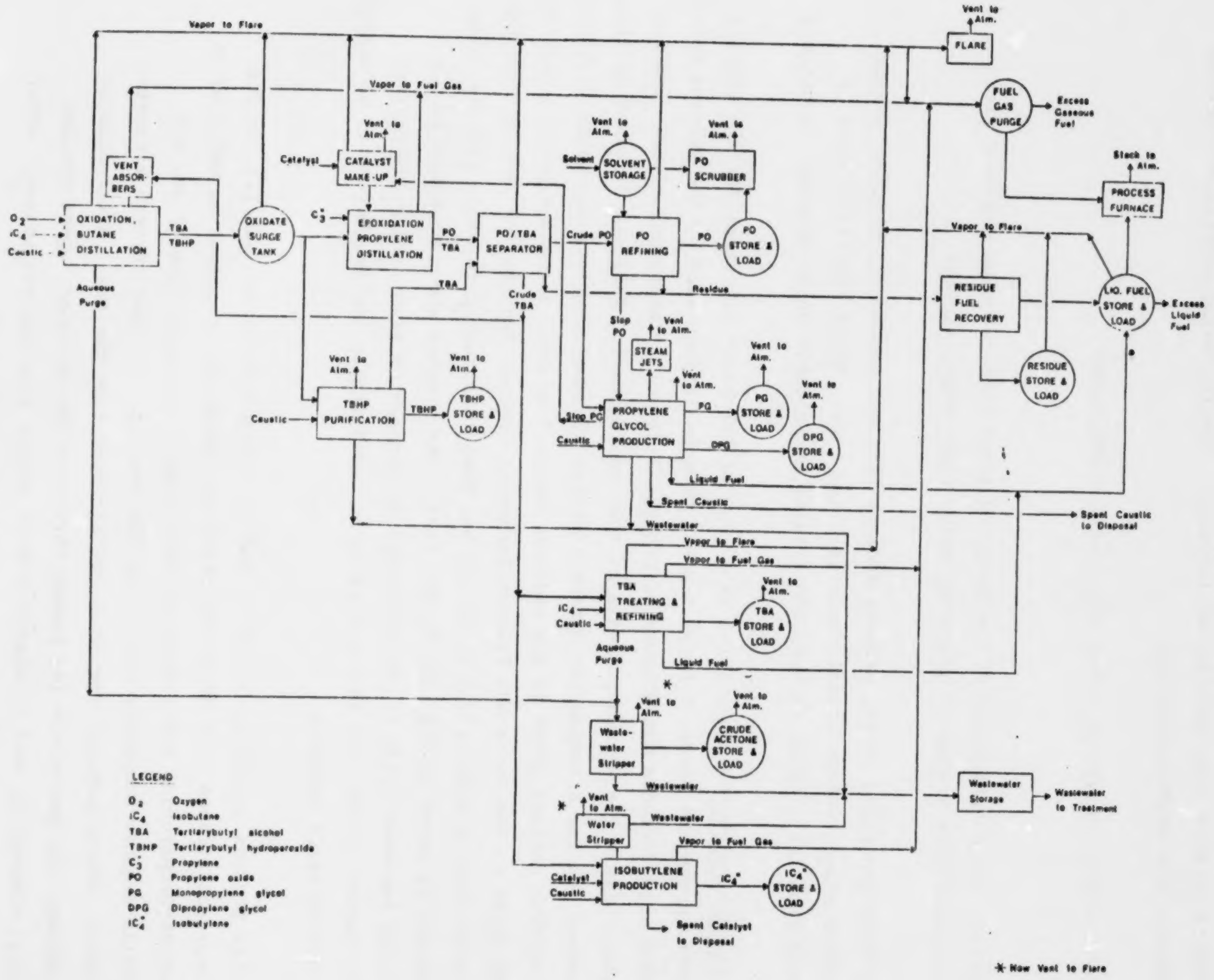

Vapor to Flare
Vapor to Fuel Gas
Vent to Atm.
FLARE
FUEL GAS PURGE
Excess Gaseous Fuel
Stack to Atm.
PROCESS FURNACE
VENT ABSORBERS
O_2
iC_4
Caustic
OXIDATION, BUTANE DISTILLATION
TBA
TBHP
Aqueous Purge
OXIDATE SURGE TANK
Catalyst
CATALYST MAKE-UP
$C_3^=$
EPOXIDATION PROPYLENE DISTILLATION
PO
TBA
PO/TBA SEPARATOR
Crude TBA
Crude PO
Solvent
SOLVENT STORAGE
PO SCRUBBER
PO REFINING
PO STORE & LOAD
Residue
Slop PO
STEAM JETS
RESIDUE FUEL RECOVERY
RESIDUE STORE & LOAD
LIQ. FUEL STORE & LOAD
Excess Liquid Fuel
TBHP PURIFICATION
TBHP STORE & LOAD
Slop PO
PROPYLENE GLYCOL PRODUCTION
PG
PG STORE & LOAD
DPG
DPG STORE & LOAD
Liquid Fuel
Spent Caustic
Spent Caustic to Disposal
Wastewater
TBA TREATING & REFINING
TBA STORE & LOAD
Aqueous Purge
*
Waste-water Stripper
CRUDE ACETONE STORE & LOAD
Wastewater Storage
Wastewater to Treatment
Water Stripper
ISOBUTYLENE PRODUCTION
$iC_4^=$
$iC_4^=$ STORE & LOAD
Spent Catalyst to Disposal
LEGEND
O_2 Oxygen
iC_4 Isobutane
TBA Tertiarybutyl alcohol
TBHP Tertiarybutyl hydroperoxide
$C_3^=$ Propylene
PO Propylene oxide
PG Monopropylene glycol
DPG Dipropylene glycol
$iC_4^=$ Isobutylene
* Now Vent to Flare

Fig. III-3. Block Flow Diagram for Oxirane, Bayport, TX, Manufacture of PO Via t-Butyl Hydroperoxide

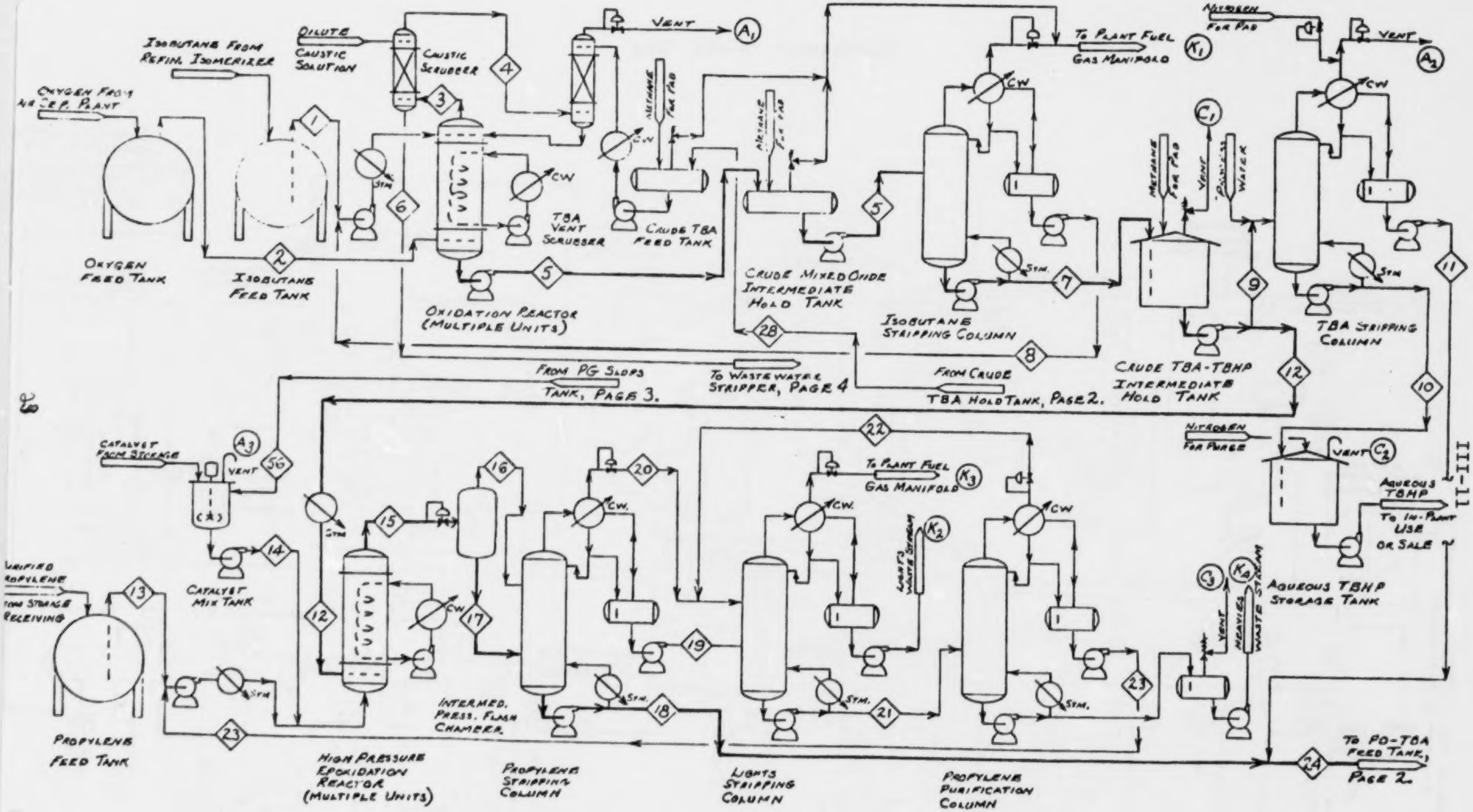

OXYGEN FROM AIR SEP. PLANT
OXYGEN FEED TANK
ISOBUTANE FROM REFIN. ISOMERIZER
ISOBUTANE FEED TANK
DILUTE CAUSTIC SOLUTION
CAUSTIC SCRUBBER
1
2
3
4
5
6
STM
CW
OXIDATION REACTOR (MULTIPLE UNITS)
TBA VENT SCRUBBER
VENT
A1
CRUDE TBA FEED TANK
METHANE FOR PAD
METHANE FOR PAD
CRUDE MIXED OXIDE INTERMEDIATE HOLD TANK
5
28
ISOBUTANE STRIPPING COLUMN
CW
STM.
7
8
TO PLANT FUEL GAS MANIFOLD
K1
FROM CRUDE TBA HOLD TANK, PAGE 2.
TO WASTE WATER STRIPPER, PAGE 4
FROM PG SLOPS TANK, PAGE 3.
METHANE FOR PAD
VENT
C1
PROCESS WATER
9
CRUDE TBA-TBHP INTERMEDIATE HOLD TANK
12
NITROGEN FOR PAD
VENT
A2
CW
STM
TBA STRIPPING COLUMN
11
10
NITROGEN FOR PURGE
VENT
C2
AQUEOUS TBHP TO IN-PLANT USE OR SALE
AQUEOUS TBHP STORAGE TANK
CATALYST FROM STORAGE
A3
VENT
56
CATALYST MIX TANK
14
URIFIED ROPYLENE ION STORAGE RECEIVING
13
PROPYLENE FEED TANK
STM
23
12
STM
15
CW
HIGH PRESSURE EPOXIDATION REACTOR (MULTIPLE UNITS)
16
17
INTERMED. PRESS. FLASH CHAMBER
20
CW.
STM.
18
19
PROPYLENE STRIPPING COLUMN
22
TO PLANT FUEL GAS MANIFOLD
K3
CW.
LIGHTS WASTE STREAM
K2
STM.
21
LIGHTS STRIPPING COLUMN
CW
STM.
23
PROPYLENE PURIFICATION COLUMN
C3
VENT
K4
HEAVIES WASTE STREAM
24
TO PO-TBA FEED TANK, PAGE 2.

Fig. III-4. Model Plant (Uncontrolled) for PO via t-Butyl Hydroperoxide

(Page 1 of 4)

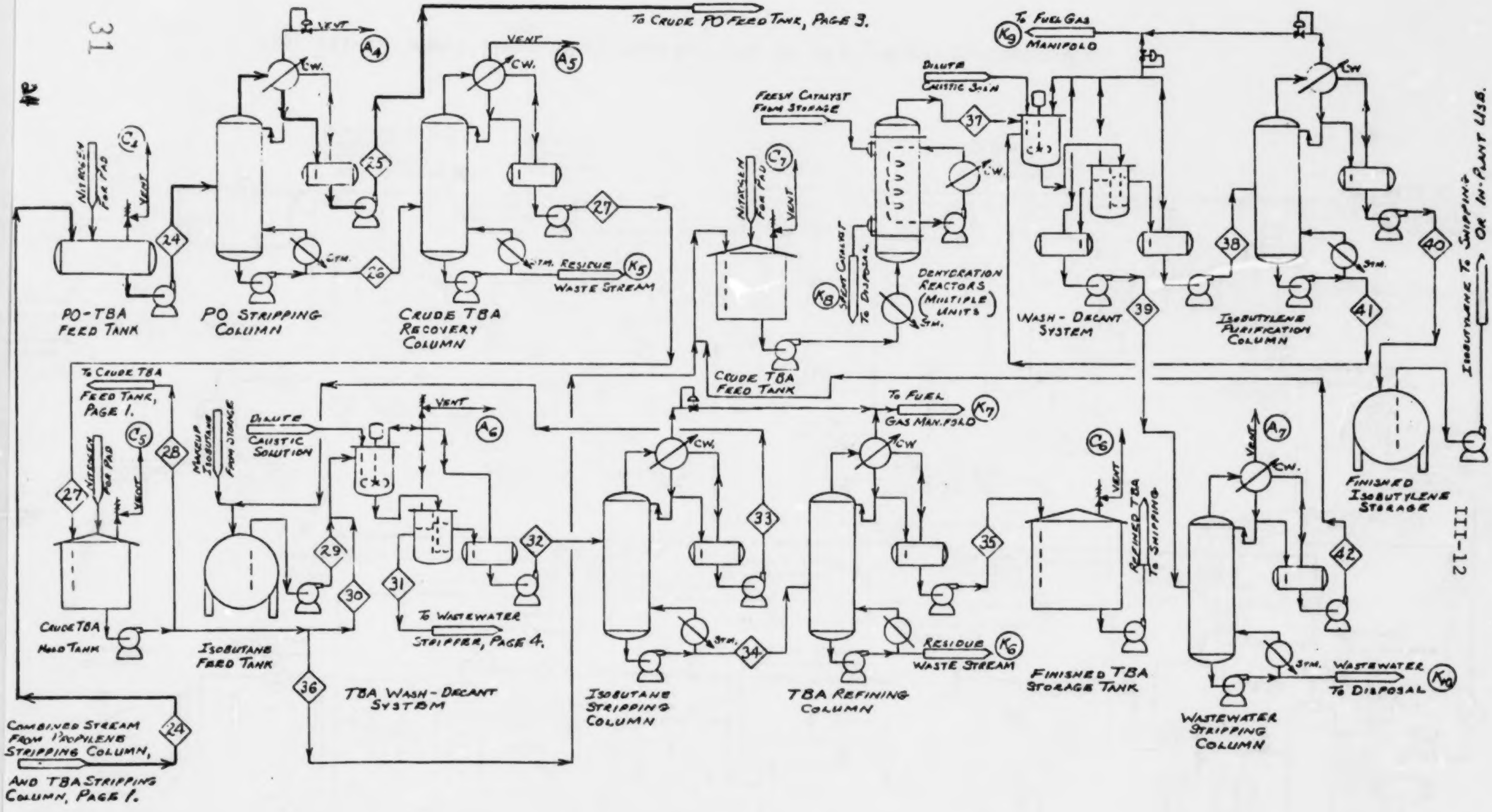

To Crude PO Feed Tank, Page 3.
Nitrogen For Pad
Vent
C4
A4
A5
CW.
STM.
24
25
26
27
K5
Residue
Waste Stream
PO-TBA Feed Tank
PO Stripping Column
Crude TBA Recovery Column
C7
Crude TBA Feed Tank
Fresh Catalyst From Storage
Spent Catalyst To Disposal
K8
Dilute Caustic Sol'n
37
Dehydration Reactors (Multiple Units)
K9
To Fuel Gas Manifold
Wash - Decant System
38
39
40
41
Isobutylene Purification Column
Isobutylene To Shipping Or In-Plant Use.
Finished Isobutylene Storage
To Crude TBA Feed Tank, Page 1.
C5
28
27
Crude TBA Hold Tank
Makeup Isobutane From Storage
Dilute Caustic Solution
Isobutane Feed Tank
29
30
31
A6
To Wastewater Stripper, Page 4.
32
36
TBA Wash - Decant System
Combined Stream From Propylene Stripping Column, And TBA Stripping Column, Page 1.
24
33
34
Isobutane Stripping Column
To Fuel Gas Manifold
K7
35
TBA Refining Column
Residue
Waste Stream
K6
C6
Refined TBA To Shipping
Finished TBA Storage Tank
A7
42
Wastewater To Disposal
K10
Wastewater Stripping Column

Fig. III-4. (Continued)

(Page 2 of 4)

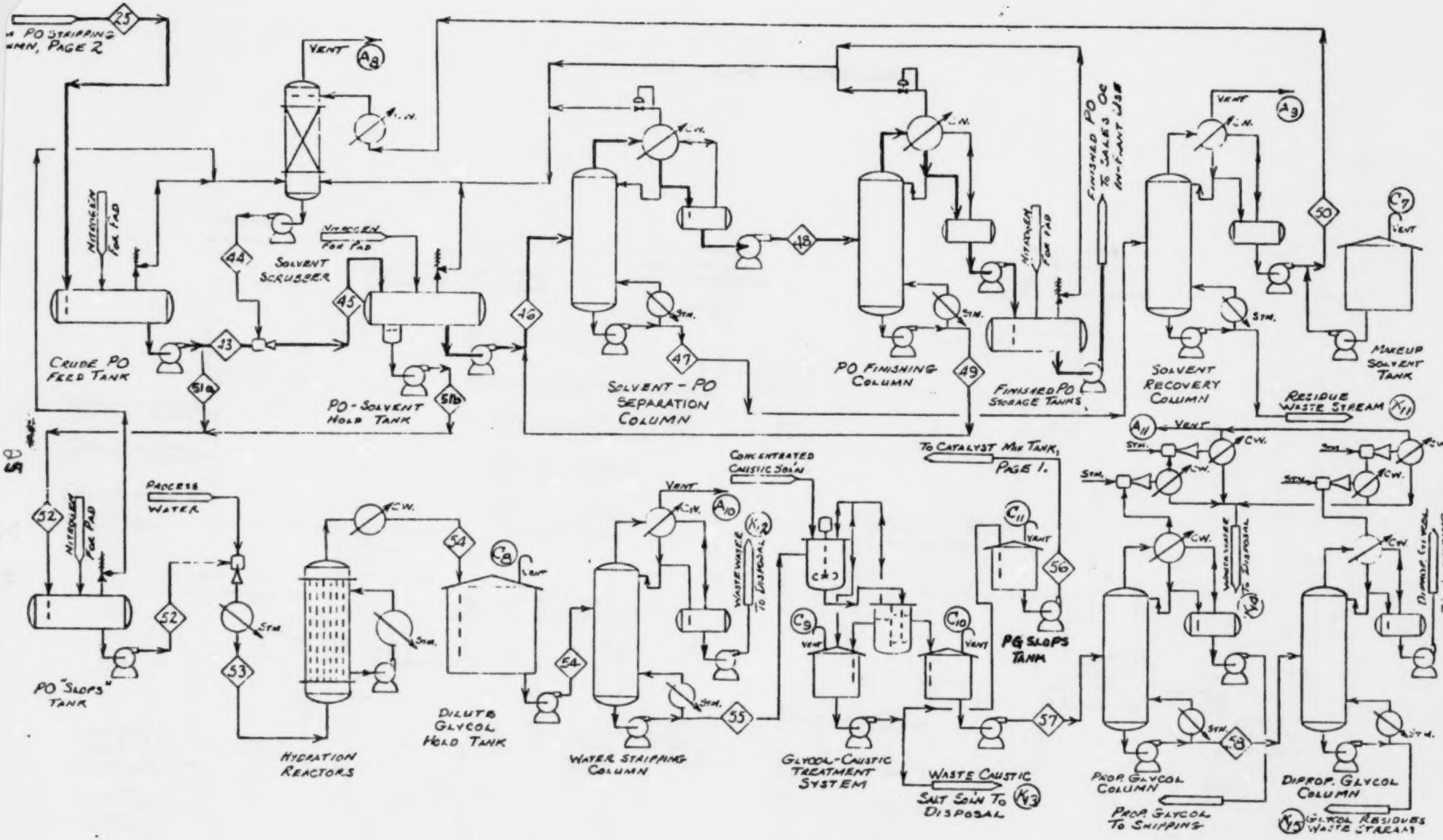

PO STRIPPING
…MN, PAGE 2
25
VENT
A8
C.W.
NITROGEN FOR PAD
CRUDE PO FEED TANK
43
44
SOLVENT SCRUBBER
NITROGEN FOR PAD
45
PO - SOLVENT HOLD TANK
51a
51b
46
C.W.
STM.
47
SOLVENT - PO SEPARATION COLUMN
48
C.W.
STM.
PO FINISHING COLUMN
49
NITROGEN FOR PAD
FINISHED PO STORAGE TANKS
FINISHED PO TO SALES OR IN-PLANT USE
VENT
A9
C.W.
STM.
SOLVENT RECOVERY COLUMN
50
C7
VENT
MAKEUP SOLVENT TANK
RESIDUE WASTE STREAM
X11
52
NITROGEN FOR PAD
PO "SLOPS" TANK
52
PROCESS WATER
STM.
53
HYDRATION REACTORS
C.W.
STM.
54
C8
VENT
DILUTE GLYCOL HOLD TANK
54
VENT
C.W.
A10
X12
WASTEWATER TO DISPOSAL
STM.
WATER STRIPPING COLUMN
55
CONCENTRATED CAUSTIC SOL'N
C9
VENT
C10
VENT
GLYCOL-CAUSTIC TREATMENT SYSTEM
WASTE CAUSTIC SALT SOL'N TO DISPOSAL
X13
TO CATALYST MIX TANK, PAGE 1.
C11
VENT
56
PG SLOPS TANK
57
A11
VENT
STM.
C.W.
STM.
C.W.
C.W.
WASTE WATER TO DISPOSAL
STM.
58
PROP. GLYCOL COLUMN
PROP. GLYCOL TO SHIPPING
DIPROP. GLYCOL TO SHIPPING
C.W.
STM.
DIPROP. GLYCOL COLUMN
X15
GLYCOL RESIDUES WASTE STREAM

Fig. III-4. (Continued)

(Page 3 of 4)

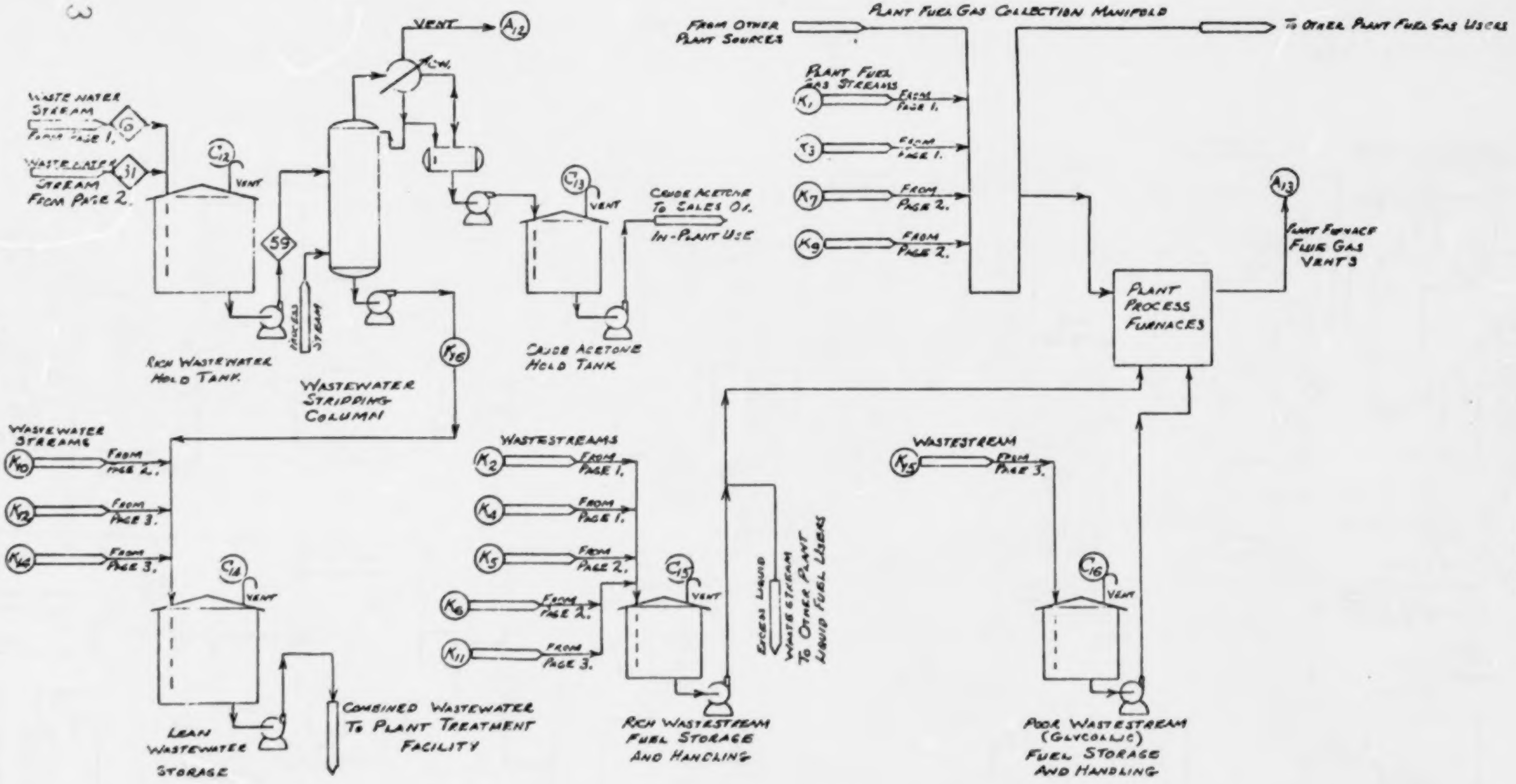

VENT
A12
C.W.
WASTEWATER STREAM FROM PAGE 1.
G
WASTEWATER STREAM FROM PAGE 2.
31
C12
VENT
59
PROCESS STEAM
RICH WASTEWATER HOLD TANK
WASTEWATER STRIPPING COLUMN
K16
C13
VENT
CRUDE ACETONE TO SALES OR IN-PLANT USE
CRUDE ACETONE HOLD TANK
FROM OTHER PLANT SOURCES
PLANT FUEL GAS COLLECTION MANIFOLD
TO OTHER PLANT FUEL GAS USERS
PLANT FUEL GAS STREAMS
K1
FROM PAGE 1.
K3
FROM PAGE 1.
K7
FROM PAGE 2.
K9
FROM PAGE 2.
A13
PLANT FURNACE FLUE GAS VENTS
PLANT PROCESS FURNACES
WASTEWATER STREAMS
K10
FROM PAGE 2.
K12
FROM PAGE 3.
K14
FROM PAGE 3.
C14
VENT
LEAN WASTEWATER STORAGE
COMBINED WASTEWATER TO PLANT TREATMENT FACILITY
WASTESTREAMS
K2
FROM PAGE 1.
K4
FROM PAGE 1.
K5
FROM PAGE 2.
K6
FROM PAGE 2.
K11
FROM PAGE 3.
C15
VENT
RICH WASTESTREAM FUEL STORAGE AND HANDLING
EXCESS LIQUID WASTESTREAM TO OTHER PLANT LIQUID FUEL USERS
WASTESTREAM
K15
FROM PAGE 3.
C16
VENT
POOR WASTESTREAM (GLYCOLIC) FUEL STORAGE AND HANDLING

Fig. III-4. (Continued)

(Page 4 of 4)

The liquid stream (5) from the oxidation reactors contains t-butylhydroperoxide, t-butyl alcohol, unreacted isobutane, and various impurities. This stream (5) is sent to an isobutane stripping column, where the unreacted isobutane (8) is recovered and recycled to the oxidation reactors. The vent gas (K_1) from the isobutane stripping column is rich in isobutane and other flammable hydrocarbon vapors. This vent gas is injected into the plant fuel gas manifold for use as fuel. The bottoms stream (7) from the isobutane stripping column contains the crude mixture of t-butylhydroperoxide and t-butyl alcohol, and is stored in an intermediate hold tank.

From the intermediate hold tank a side stream (9) of the crude mixture is sent to a TBA stripping column, where process water is added and an azeotropic mixture of t-butyl alcohol and water (11) is separated overhead. Vent gas (A_2) from this column contains nitrogen, water vapor, t-butyl alcohol vapor, and other VOC. The bottoms stream (10) from this column consists of a mixture of t-butylhydroperoxide (70%) in water (30%), along with some residual impurities. This bottoms stream (10) is stored for sale or for in-plant use.

The main-product stream (12) from the intermediate hold tank is heated and fed to the high-pressure epoxidation reactors, along with the feed streams (13 and 23) of propylene and a small feed stream (14) of catalyst in propylene glycol "slops."* A minor process vent gas stream (A_3) discharges from the catalyst mix tank. The reaction mixture (15) is discharged to an intermediate-pressure flash chamber. Some of the unreacted propylene (16) exits the flash chamber as vapor and is fed as a vapor stream to the upper section of the propylene stripping column. The liquid stream (17) from the flash chamber is fed to the lower section of the propylene stripping column.

The propylene stripping column removes the unreacted propylene (and other low-boiling-point hydrocarbons) from the main-product stream. The vent gas (20) from this column is fed as a vapor stream to the upper section of the lights stripping column, while the overhead condensate (19) is fed as a liquid to the lower section of the lights stripping column. The bottoms stream (18) from the propylene stripping column contains propylene oxide, t-butyl alcohol, and reaction residues and impurities.

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*In this process the manufacturer uses the term slop to define a crude mixture of propylene glycol contaminated predominantly with water and dipropylene glycol.

The lights stripping column separates the low-boiling-point hydrocarbons and other impurities from the recycle propylene stream. The vent gas (K_3) from the column contains highly flammable hydrocarbons such as methane, ethane, ethylene, etc., and is injected into the plant fuel gas manifold. The overhead condensate stream (K_2) also contains a portion of these flammable hydrocarbons, as well as some propylene. This stream can either be collected and stored under pressure for use as a liquid fuel or be vaporized and fed into the plant fuel gas manifold. The bottoms stream (21) from this column is rich in propylene, propane, and some other higher boiling point hydrocarbons. This bottoms stream (21) is fed to the propylene purification column.

The propylene purification column is used to separate the recycle propylene stream (23) from the higher boiling point components. The vent gas (22) from this column is injected as a vapor into the upper section of the lights stripping column for recovery of the propylene contained in the vapor. The bottoms stream (K_4) from the propylene purification column contains propane and other higher boiling point hydrocarbons. This material can either be collected and stored under pressure for use as a liquid fuel or be vaporized and injected into the plant fuel gas manifold.

The crude t-butyl alcohol stream (11) from the TBA stripping column is combined with the main-product stream (18) from the bottom of the propylene stripping column. This combined stream (24) is held in the PO-TBA feed tank for delivery to the propylene oxide (PO) stripping column. The PO stripping column separates the crude propylene oxide (25) from the t-butyl alcohol stream (26) containing the process residues. The vent gas stream from this PO stripping column is labeled A_4.

The bottoms stream (26) from the PO stripping column is fed to a crude TBA recovery column. In this column crude t-butyl alcohol is separated as an overhead water-alcohol azeotrope stream (27) from the bottoms residue stream (K_5) containing the catalyst residues and some high-boiling-point organic compounds.

The crude t-butyl alcohol (27) is held in a crude TBA hold tank. One portion of this t-butyl alcohol is fed as a stream (28) to the crude TBA feed tank for use as the scrubbing fluid in the TBA vent scrubber. Another portion is fed as a stream (30) to the TBA wash-decant system, along with a stream (29) of recycled isobutane. This mixed stream enters the TBA wash-decant system, where it is contacted with a dilute caustic solution for reaction with and removal of carbonyl impurities from the isobutane-t-butyl alcohol mixture. After separation, the water layer (31) containing the sodium salts and dissolved carbonyl compounds is sent to the wastewater stripper, while the organic layer (32) is sent to the isobutane stripping column. In the isobutane stripping column the isobutane (33) is separated from the mixture and recycled to the isobutane feed tank. The t-butyl alcohol bottoms stream (34) is fed to the TBA refining column, where purified t-butyl alcohol (35) is recovered overhead and stored for shipping as one of the principal products of this facility. The bottoms stream (K_6) from the TBA refining column contains residual high-boiling-point impurities and can be collected and treated for use as a liquid fuel. The vent gases from both columns are collected as a single vent stream (K_7) and injected into the plant fuel gas manifold.

A third portion of the crude t-butyl alcohol (36) is sent to a crude TBA feed tank, where it is combined with a recycle TBA stream (42) as a feed stream to the dehydration reactors. In the dehydration reactors the t-butyl alcohol is converted to a crude mixture of water, isobutylene, and residual t-butyl alcohol. This reaction mixture (37) is treated with dilute caustic in a wash-decant system for removal of carbonyl impurities and unreacted t-butyl alcohol. The aqueous stream (39) is sent to a wastewater stripping column, where an azeotropic mixture of residual t-butyl alcohol and water (42) is recovered and recycled to the crude TBA feed tank. The vent gas stream from the wastewater stripping column is labeled A_7. The stripped wastewater stream (K_{10}) is sent to the plant wastewater treatment facility. The isobutylene purification column receives the organic layer (38) from the wash-decant system and recovers purified isobutylene (40) from this organic stream. The bottoms stream (41) from the isobutylene purification column contains some unreacted t-butyl alcohol and minor impurities. The bottoms stream (41) is recycled to the wash-decant system for extraction of these materials. The vent gas from the isobutylene purification column, along with any vent gas from the wash-decant system, is combined as vent gas stream K_9 and sent to the plant fuel gas manifold.

The crude propylene oxide (25) from the PO stripping column is held in the crude PO feed tank. The main stream (43) from this tank is blended with the solvent stream (44) from the solvent scrubber and held in the PO solvent hold tank. This combined stream (46) of mixed PO and solvent is fed to the solvent-PO separation column, where a purified propylene oxide stream (48) is separated from the solvent stream (47) containing the higher boiling point impurities. The vent gas from the separation column is combined with other vent gas streams going to the solvent scrubber. The propylene oxide stream (48) from the separation column is given a final purification step in the PO finishing column to separate high-purity finished propylene oxide from the higher boiling point bottoms stream (49). Stream 49 is recycled to the solvent-PO separation column. The vent gas from the PO finishing column is combined with other vent gas streams going to the solvent scrubber. The high-purity finished propylene oxide is stored prior to shipment. The solvent-rich stream (47) from the solvent-PO separation column is sent to a solvent recovery column for separation of purified solvent (50) from the residue stream (K_{11}). The vent stream from the solvent recovery column is labeled A_9. The purified solvent stream is chilled and used as scrubber liquid in the solvent scrubber, where it strips most of the propylene oxide out of the combined vent gas stream. The vent gas discharged from the solvent scrubber is labeled A_8.

An aqueous layer (51_b) containing some dissolved propylene oxide is drained from the bottom of the PO-solvent hold tank. This stream is combined with a side stream (51_a) of crude propylene oxide from the crude PO feed tank. This combined stream (52) is mixed with process water, heated, and fed to the hydration reactors for conversion of the propylene oxide to a mixture of propylene glycol, dipropylene glycol, and miscellaneous glycolic residues dissolved in excess water. The reaction mixture (54) is fed from a dilute glycol hold tank to the water stripping column. In this column the wastewater stream (K_{12}) is taken off overhead and sent to the plant wastewater treatment system. The vent gas stream from this column is labeled A_{10}. The bottoms (55) from this column are sent to a glycol-caustic treatment system, where the crude glycol is treated with a concentrated caustic solution to react with and remove acidic (carbonyl) organic materials. The aqueous layer is collected in a hold tank, where propylene glycol (PG) slops are separated from the caustic-salt solution. The PG slops are collected in a separate tank, and the PG slops stream (56) is used as the

37

liquid in the catalyst mix tank. After separation, the waste caustic-salt solution (K_{13}) is sent to the plant waste treatment facilities.

The main organic stream (57) from the glycol caustic treatment system is sent to a propylene glycol column, where the main-product stream of propylene glycol is distilled under vacuum, with steam vacuum jets and condensers used as the vacuum source. The bottoms stream (58) from the propylene glycol column is distilled under vacuum (steam jets and condensers) in the dipropylene glycol column to yield a secondary-product stream of dipropylene glycol and a bottoms waste stream (K_{15}) of glycolic residues. The vent gases from the vacuum steam jets on these two columns are combined and discharged as vent gas stream A_{11}. The condensate from the jet condensers is combined and discharged as the wastewater stream (K_{14}).

The rich wastewater streams (6) from the caustic scrubber and (31) from the TBA wash-decant system are collected in the rich wastewater collection tank and fed as a combined stream (59) to the wastewater stripping column. In this column crude acetone is stripped out of the wastewater and stored for sale or in-plant use. The vent gas stream from this column is labeled A_{12}. The stripped wastewater stream (K_{16}) from this column is combined with the other wastewater streams (K_{10}, K_{12}, and K_{14}), stored, and sent to the plant wastewater treatment system.

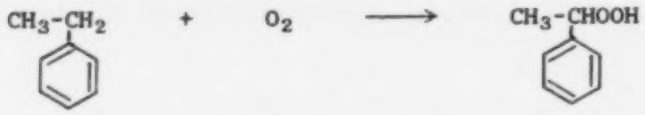
Vent gas streams rich in flammable hydrocarbons (K_1, K_3, K_7, and K_9) are collected in the plant fuel gas header, compressed as required, and fed to the plant process furnaces and other fuel gas users for combustion. The resultant flue gases are discharged to the atmosphere.

Process waste streams rich in flammable liquids with high heating values (K_2, K_4, K_5, K_6, and K_{11}) are collected, stored, treated as required, and fed to the plant process furnaces and other liquid fuel consumers for combustion. Since these waste liquid (fuel) streams do not contain troublesome components and burn cleanly, the flue gases from combustion of these materials in the process furnaces is vented to the atmosphere as flue gas.

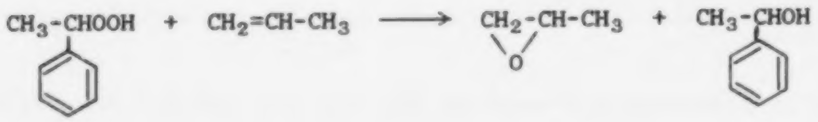
The glycolic waste stream (K_{15}) is also collected, stored, and fed to the process furnace as a fuel stream. Glycolic wastes have a relatively low heating value and do not burn well by themselves, but they also burn cleanly when combusted in a high-temperature fire chamber in the presence of other high-heating-value fuels, permitting the resultant flue gases to be discharged to the atmosphere.

3. Ethylbenzene Hydroperoxidation Process

a. Process Chemistry—In the first major process step purified ethylbenzene is reacted with oxygen from the air to form a dilute solution of ethylbenzene hydroperoxide in unreacted ethylbenzene. This conversion is represented by the following simplified equation:



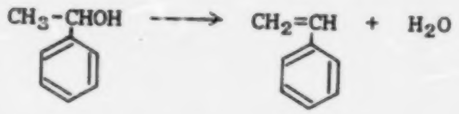
In the second major process step the ethylbenzene hydroperoxide solution is concentrated by some of the residual ethylbenzene being evaporated, and this concentrated solution is then used to epoxidize propylene to propylene oxide in the presence of an epoxidation promotion catalyst. A simplified equation representing this epoxidation step is as follows:



The principal coproduct of this epoxidation reaction is α-methyl benzyl alcohol. Some acetophenone is also produced as a by-product in this reaction sequence, along with minor amounts of various other oxidation products, usually acidic in nature.

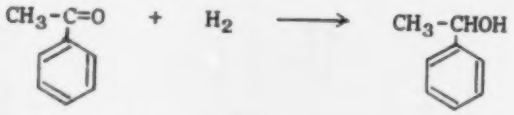
After the propylene is epoxidized to propylene oxide, distillation techniques are used to separate unreacted propylene (for recycle), propylene oxide product, and a mixed stream of unreacted ethylbenzene, α-methyl benzyl alcohol, and acetophenone. A caustic wash is used to remove acidic impurities, and the mixed stream is further distilled to remove the ethylbenzene from the mixture of α-methyl benzyl alcohol and acetophenone. Purified ethylbenzene is recycled to the ethylbenzene hydroperoxide step in the process.

The third major process step is the dehydration of the α-methyl benzyl alcohol to styrene monomer in the presence of a dehydration catalyst. The acetophenone passes through this reaction step without being reacted. A simplified equation for this dehydration reaction is as follows:



Additional distillation steps are used to separate the styrene monomer from the unreacted acetophenone and to purify the styrene monomer to polymerization-grade monomer for sale.

The final major process step is the hydrogenation of the acetophenone by-product to α-methyl benzyl alcohol. In this process step the acetophenone residue from the styrene monomer distillation operation is reacted with hydrogen gas in the presence of a hydrogenation catalyst. The following simplified equation represents this hydrogenation step:



After hydrogenation the crude α-methyl benzyl alcohol formed by the reaction of the acetophenone with hydrogen is recycled to the process for conversion to styrene monomer.

b. Process Technology——Figure III-5 is a copy of the block flowsheet for the Oxirane, Channelview, propylene oxide—styrene monomer process as furnished by the Oxirane Corp.[9] Based on this flowsheet and the accompanying nonconfidential information described in the trip report,[9] as well as on the process descriptions given in the three SRI Process Economics Program Reports[2—4] and on physical property data, a model plant has been constructed for this process, as shown in Fig. III-6, pp. 1—3. The process shown is probably not an exact representation of this peroxidation process as practiced by Oxirane at their Channelview plant but is believed to be sufficiently representative to be useful for air emission purposes.

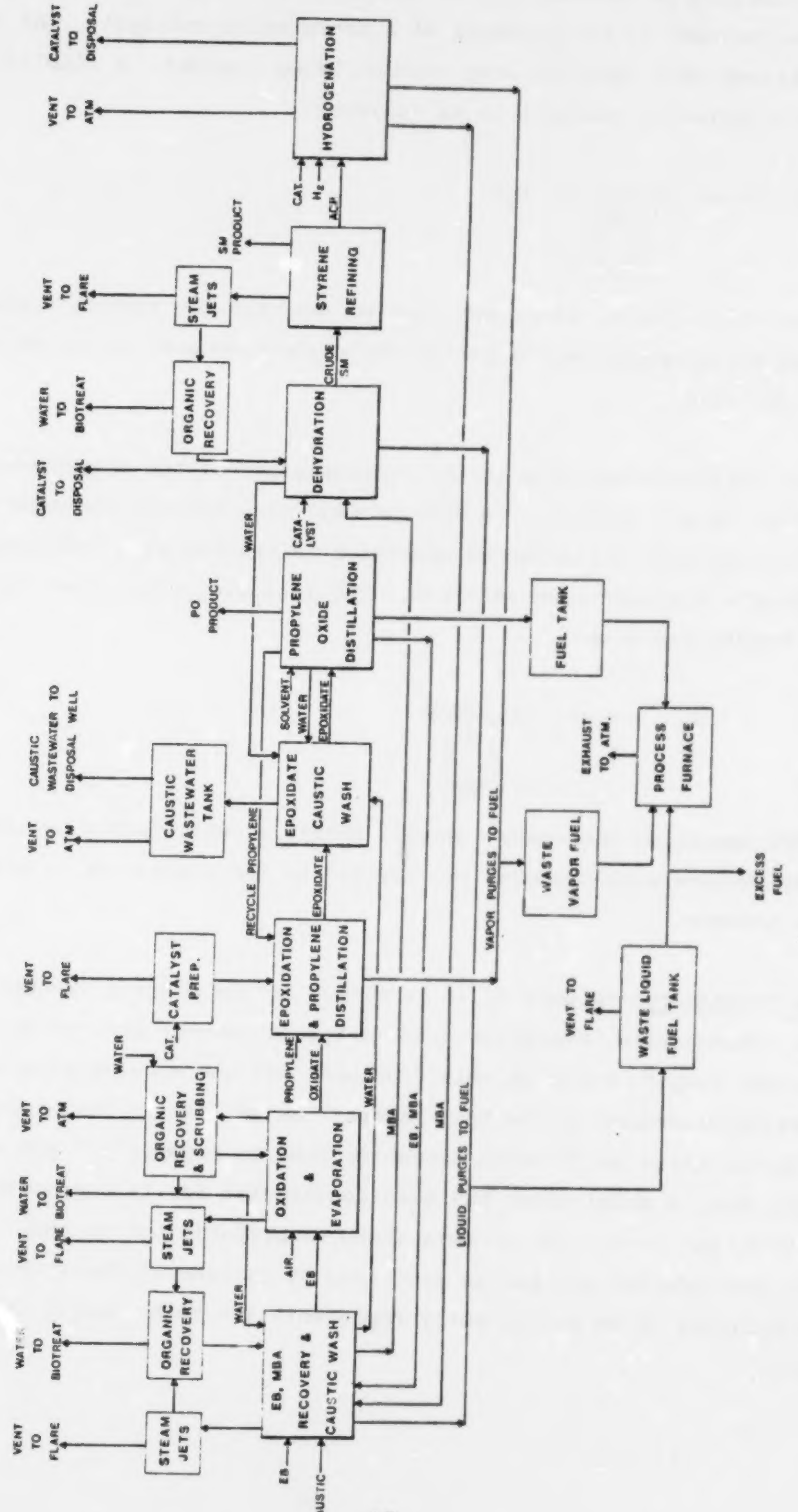

VENT TO FLARE
STEAM JETS
WATER TO BIOTREAT
ORGANIC RECOVERY
VENT TO FLARE
STEAM JETS
WATER TO BIOTREAT
VENT TO ATM
ORGANIC RECOVERY & SCRUBBING
WATER
CAT.
VENT TO FLARE
CATALYST PREP.
VENT TO ATM
CAUSTIC WASTEWATER TANK
CAUSTIC WASTEWATER TO DISPOSAL WELL
PO PRODUCT
CATALYST TO DISPOSAL
WATER TO BIOTREAT
ORGANIC RECOVERY
VENT TO FLARE
STEAM JETS
SM PRODUCT
VENT TO ATM
CATALYST TO DISPOSAL
EB
CAUSTIC
EB, MBA RECOVERY & CAUSTIC WASH
WATER
AIR
EB
OXIDATION & EVAPORATION
PROPYLENE
OXIDATE
WATER
EPOXIDATION & PROPYLENE DISTILLATION
RECYCLE PROPYLENE
EPOXIDATE
EPOXIDATE CAUSTIC WASH
SOLVENT
WATER
EPOXIDATE
PROPYLENE OXIDE DISTILLATION
WATER
CATA-LYST
DEHYDRATION
CRUDE SM
STYRENE REFINING
CAT.
H_2
ACP
HYDROGENATION
MBA
EB, MBA
MBA
LIQUID PURGES TO FUEL
VAPOR PURGES TO FUEL
FUEL TANK
WASTE VAPOR FUEL
VENT TO FLARE
WASTE LIQUID FUEL TANK
EXHAUST TO ATM.
PROCESS FURNACE
EXCESS FUEL

Fig. III-5. Oxirane, Channelview, TX, Propylene Oxide-Styrene Monomer Process Flow Diagram

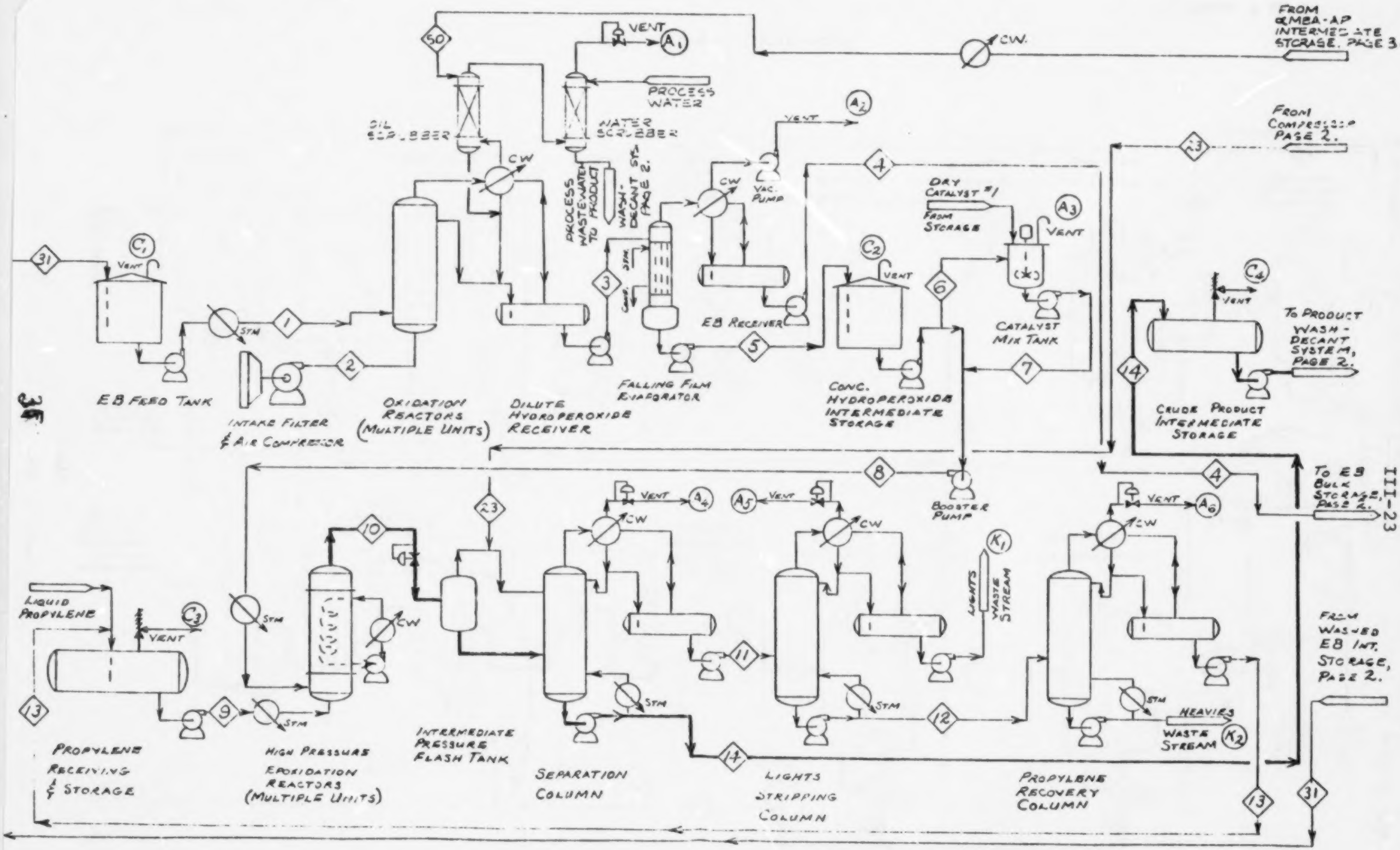

FROM αMBA-AP INTERMEDIATE STORAGE, PAGE 3.
CW.
50
VENT
A1
PROCESS WATER
OIL SCRUBBER
WATER SCRUBBER
CW
PROCESS WASTEWATER TO PRODUCT WASH-DECANT SYS. PAGE 2.
VENT
A2
VAC. PUMP
CW
FROM COMPRESSOR PAGE 2.
23
4
DRY CATALYST #1
FROM STORAGE
A3
VENT
31
C1
VENT
STM
1
2
3
STM
COND.
EB RECEIVER
C2
VENT
6
C4
VENT
TO PRODUCT WASH-DECANT SYSTEM, PAGE 2.
5
7
CATALYST MIX TANK
14
EB FEED TANK
INTAKE FILTER & AIR COMPRESSOR
OXIDATION REACTORS (MULTIPLE UNITS)
DILUTE HYDROPEROXIDE RECEIVER
FALLING FILM EVAPORATOR
CONC. HYDROPEROXIDE INTERMEDIATE STORAGE
CRUDE PRODUCT INTERMEDIATE STORAGE
8
BOOSTER PUMP
4
TO EB BULK STORAGE, PAGE 2.
23
10
VENT
A4
CW
A5
VENT
CW
VENT
A6
CW
K1
LIGHTS WASTE STREAM
LIQUID PROPYLENE
VENT
C3
STM
CW
11
FROM WASHED EB INT. STORAGE, PAGE 2.
13
9
STM
STM
STM
12
STM
HEAVIES
WASTE STREAM
K2
14
PROPYLENE RECEIVING & STORAGE
HIGH PRESSURE EPOXIDATION REACTORS (MULTIPLE UNITS)
INTERMEDIATE PRESSURE FLASH TANK
SEPARATION COLUMN
LIGHTS STRIPPING COLUMN
PROPYLENE RECOVERY COLUMN
13
31

Fig. III-6. Model Plant (Uncontrolled) for PO by EB Hydroperoxide

(Page 1 of 3)

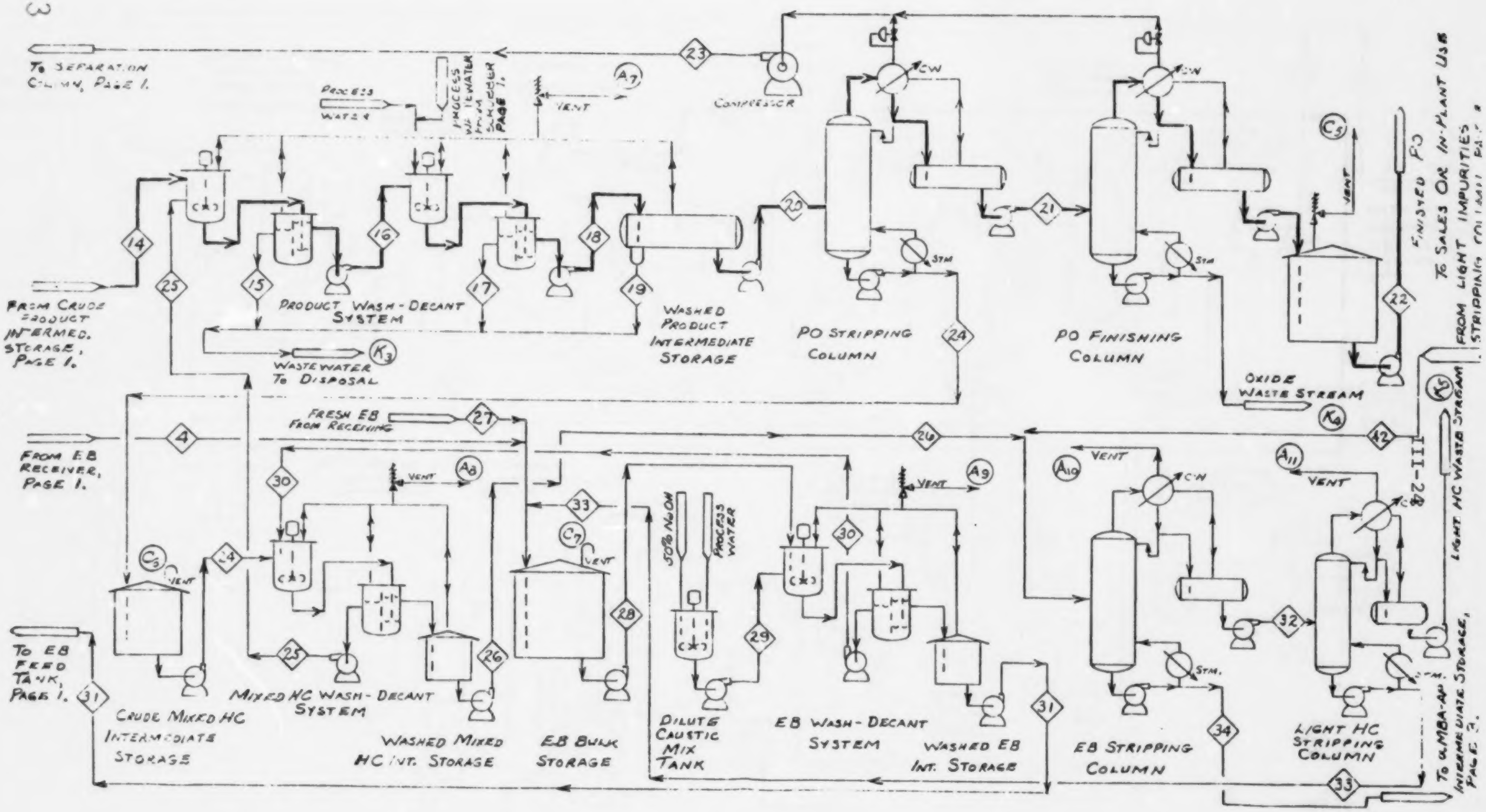

To SEPARATION COLUMN, PAGE 1.
23
COMPRESSOR
A7
VENT
PROCESS WATER
PROCESS WATER FROM SCRUBBER PAGE 1.
CW
C5
VENT
FINISHED PO
TO SALES OR IN-PLANT USE
FROM LIGHT IMPURITIES STRIPPING COLUMN PAGE 3
14
25
15
16
17
18
19
20
21
22
24
FROM CRUDE PRODUCT INTERMED. STORAGE, PAGE 1.
PRODUCT WASH-DECANT SYSTEM
WASHED PRODUCT INTERMEDIATE STORAGE
PO STRIPPING COLUMN
PO FINISHING COLUMN
STM
OXIDE WASTE STREAM
K4
K5
WASTEWATER To DISPOSAL
K3
FRESH EB FROM RECEIVING
27
4
26
42
FROM EB RECEIVER, PAGE 1.
30
A8
VENT
33
C7
VENT
50% NaOH
PROCESS WATER
A9
VENT
30
A10
VENT
CW
A11
VENT
LIGHT HC WASTE STREAM
C3
VENT
24
25
26
28
29
31
32
34
33
To EB FEED TANK, PAGE 1.
31
CRUDE MIXED HC INTERMEDIATE STORAGE
MIXED HC WASH-DECANT SYSTEM
WASHED MIXED HC INT. STORAGE
EB BULK STORAGE
DILUTE CAUSTIC MIX TANK
EB WASH-DECANT SYSTEM
WASHED EB INT. STORAGE
EB STRIPPING COLUMN
LIGHT HC STRIPPING COLUMN
STM.
To αMBA-AP INTERMEDIATE STORAGE, PAGE 3.

Fig. III-6. (Continued)

(Page 2 of 3)

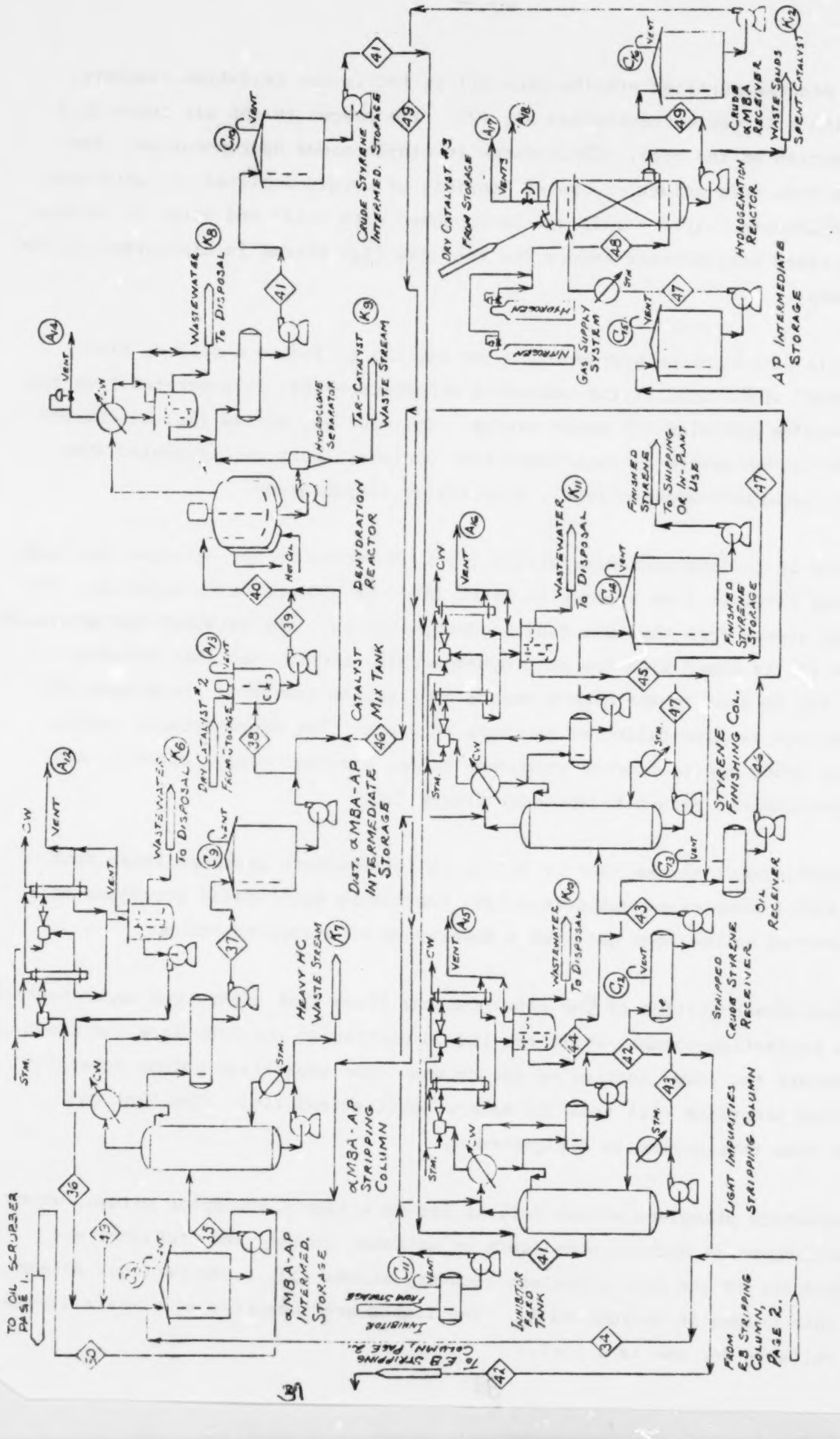

TO OIL SCRUBBER PAGE 1.
αMBA-AP INTERMED. STORAGE
αMBA-AP STRIPPING COLUMN
HEAVY HC WASTE STREAM
DIST. αMBA-AP INTERMEDIATE STORAGE
DRY CATALYST #2 FROM STORAGE
CATALYST MIX TANK
DEHYDRATION REACTOR
HOT OIL
HYDROCLONE SEPARATOR
TAR-CATALYST WASTE STREAM
WASTEWATER TO DISPOSAL
CRUDE STYRENE INTERMED. STORAGE
DRY CATALYST #3 FROM STORAGE
NITROGEN
HYDROGEN
GAS SUPPLY SYSTEM
HYDROGENATION REACTOR
CRUDE αMBA RECEIVER
WASTE SOLIDS SPENT CATALYST
AP INTERMEDIATE STORAGE
VENTS
INHIBITOR FROM STORAGE
INHIBITOR FEED TANK
To EB STRIPPING COLUMN, PAGE 2.
FROM EB STRIPPING COLUMN, PAGE 2.
LIGHT IMPURITIES STRIPPING COLUMN
STRIPPED CRUDE STYRENE RECEIVER
OIL RECEIVER
STYRENE FINISHING COL.
FINISHED STYRENE STORAGE
FINISHED STYRENE TO SHIPPING OR IN-PLANT USE
STM.
CW
VENT
A11
A12
A13
A14
A15
A16
A17
A18
C9
C10
C11
C12
C13
C14
C15
C16
C17
K6
K7
K8
K9
K10
K11
K12
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50

Fig. III-6. (Continued)

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39

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In this process purified ethylbenzene (1) is fed to the oxidation reactors, along with a stream of compressed air (2). The oxygen in the air converts a small portion of the total ethylbenzene to ethylbenzene hydroperoxide. The vent gas from this oxidation system consists of oxygen-depleted air saturated with ethylbenzene vapor. This gas is scrubbed with "oil" and water to recover the vaporized ethylbenzene before the vent gas (A_1) stream is discharged to the atmosphere.

The dilute ethylbenzene hydroperoxide stream (3) is fed to a falling film evaporator, where some of the unreacted ethylbenzene (4) is separated from the hydroperoxide solution (5) under vacuum. The vent gas stream (A_2) discharged from the vacuum system on this evaporator contains inert gas saturated with volatile organic compounds (VOC), principally ethylbenzene.

A portion of the hydroperoxide stream (6) is diverted to the catalyst mix tank, where dry catalyst from storage is mixed into the hydroperoxide solution. The vent gas stream from this mix tank is designated A_3. The catalyst-hydroperoxide mixture (7) is mixed with the main hydroperoxide stream, and this blended stream (8) is sent to the high-pressure epoxidation reactors. Propylene (9) from storage is also delivered to these reactors. The hydroperoxide reacts with the propylene to produce propylene oxide, α-methyl benzyl alcohol, and some acetophenone as a mixed-product stream (10).

The mixed-product stream (10) is fed to an intermediate pressure flash tank, along with a compressed gas stream (23) containing principally propylene that is recovered as the vent gas from a downstream PO stripping column.

The vapor-phase portion of the flow from the flash tank enters the upper section of the separation column, while the liquid portion of the flow from the flash tank enters the lower section of the column. The separation column separates unreacted propylene (11) from the main-product stream (14). The vent gas stream from this column is designated A_4.

The unreacted propylene stream (11) is fed to a lights stripping column, where low-boiling-point hydrocarbons (such as methane, ethane, and ethylene) are stripped out of the main propylene recovery stream (12). The vent gas stream from this column is designated A_5. The lights are separated as a waste stream (K_1) suitable for use as a fuel.

The main propylene recovery stream (12) is sent to a propylene recovery column, where purified propylene (13) is taken overhead for recycle to the epoxidation reactors. The vent gas stream from this column is designated as A_6. The bottoms from this column (K_2) is a waste stream containing propane and other higher boiling point hydrocarbons and is suitable for use as a fuel.

The main-product stream (14) from the separation column is held in the crude product intermediate storage tank and then fed to the product wash-decant system. A dilute caustic stream (25) is used as the first wash liquid in this system. The exhausted caustic wash stream (15) discharges to the wastewater collection manifold. The organic layer (16) is then washed with process water to extract additional impurities. After the wastewater stream (17) from this second wash stage joins the dilute caustic wastewater stream (15), the combined wastewaters (K_3) are sent to disposal. The washed product (18) is held in the washed product intermediate storage tank, where residual traces of wastewater (19) settle out and are discharged to the wastewater collection manifold. The vent gas stream from this section is labeled A_7.

The washed product stream (20) from storage is fed to the PO stripping column, where the crude propylene oxide (21) is taken overhead to separate it from the crude mixed hydrocarbon (HC) stream (24). The vent gas from this column is discharged to a vent gas header, and the combined vent gas stream from this column and the PO finishing column is compressed and the compressed gas (23) is returned to the separation column.

The crude propylene oxide (21) is fed to the PO finishing column, where the finished propylene oxide (22) is taken overhead and then sent to final-product storage and shipping. The vent gas from the PO finishing column discharges to the vent gas collection manifold, where it combines with the vent gas from the PO stripping column. The bottoms stream (K_4) from the finishing column contains the higher boiling point impurities and is discarded as a waste stream suitable for use as a fuel.

The crude mixed hydrocarbon stream (24) is washed wih a dilute caustic stream (30) in the mixed HC wash-decant system. The dilute caustic stream (25) from this system is sent to the product wash-decant system for reuse. The washed mixed HC layer (26) is held in the washed—mixed HC intermediate storage tank. The vent gas stream from this system is labeled A_8.

Ethylbenzene (EB) (27) from incoming shipments, as well as ethylbenzene (4) from the receiver on the falling film evaporator and ethylbenzene (33) from the bottoms of the light HC stripping column, is combined and stored in the EB bulk storage tank. The ethylbenzene (28) from storage is fed to the EB wash-decant system, where it is washed with a fresh dilute caustic stream (29) from the dilute caustic mix tank. THe dilute caustic stream (30) from this system is sent to the mixed HC wash-decant system for reuse. The washed ethylbenzene (31) is sent to the EB feed tank. The vent gas stream on the EB wash-decant system is labeled A_9.

After the washing step the mixed HC stream (26) is sent to the EB stripping column, along with the overhead stream (42) from the light impurities stripping column. The EB stripping column is used to separate ethylbenzene (32) from the crude α-methyl benzyl alcohol—acetophenone mixture (α-MBA—AP) (34). The vent gs stream from this column is labeled A_{10}.

The ethylbenzene (32) from the EB stripping column is sent to the light HC stripping column, where lower boiling point hydrocarbon impurities (K_5) are stripped out of the recovered ethylbenzene (33). The hydrocarbon impurities (K_5) are suitable for use as fuel. The vent gas stream from the light HC stripping column is labeled A_{11}. The recovered ethylbenzene (33) is sent to the EB bulk storage tank.

The mixed α-MBA—AP stream (34) from the EB stripping column is combined with the oil layer (36) from the decanter tank of the vacuum steam-jet condenser system and the crude α-MBA stream (49) from the crude α-MBA receiver, and this combined stream (35) is held in the α-MBA—AP intermediate storage tank for delivery to the α-MBA—AP stripping column. This column operates under vacuum to separate the mixed α-MBA—AP stream (37) from the residual heavy-hydrocarbon waste stream (K_7). The waste stream (K_7) is suitable for use as a fuel. The vacuum steam-jet condenser system on this column condenses a mixture of hydrocarbon and water. The hydrocarbon oil layer (36) is skimmed off the water layer and is recycled to the α-MBA—AP intermediate storage tank. The water layer (K_6) is sent to the plant wastewater treatment system. The vent gas stream from the column vacuum steam-jet system is labeled A_{12}.

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The distilled α-MBA—AP stream (37) is held in an intermediate storage tank. From this tank a small stream (38) is fed to the catalyst mix tank, where dry catalyst from storage is mixed into the organic material to form a catalyst-organic mixture (39). The vent gas stream from the catalyst mix tank is labeled A_{13}. The catalyst-containing stream (39) is then combined with the main α-MBA—AP feed stream and the stream (46) from the oil receiver as a feed stream (40) to the dehydration reactor. In the reactor the α-MBA is dehydrated to styrene monomer, while the AP does not react. The condenser is used to condense the water of reaction, along with some organic vapors. The hydrocarbon oil layer is skimmed off the condensate and combined with the clear organic layer from the hydroclone. Then the condensed wastewater (K_8) is sent to the plant wastewater treatment facility. The thickened mixture of exhausted catalyst and residual organic tars (K_9) is collected for disposal. The vent gas stream from this dehydration reactor is labeled A_{14}.

The crude styrene monomer stream (41) from the dehydration reactor is stored in an intermediate storage tank and then fed to the light impurities stripping column. This column operates under vacuum to strip off low-boiling-point impurities (42) from the crude styrene monomer (43). The vacuum-jet condenser system on this column condenses a mixture of water and some hydrocarbon oil. The oil layer (44) is skimmed off and sent to the oil receiver, while the wastewater (K_{10}) is sent to the plant wastewater treatment facility. The vent gas stream from the vacuum-jet system is labeled A_{15}.

The stripped styrene monomer stream (43) is fed to the styrene finishing column, where purified styrene monomer is taken overhead, condensed, and sent to the finished styrene monomer storage tanks prior to shipment. The vacuum steam jets and condensers on this column condense a mixture of water and some hydrocarbon oil. The oil layer (45) is sent to the oil receiver, while the wastewater stream (K_{11}) is sent to the plant wastewater treatment facility. The vent gas stream exhausted by the vacuum steam jets is labeled A_{16}.

The bottoms stream (47) from the styrene finishing column is held in the AP intermediate storage tank for delivery to the hydrogenation reactor. A stream of hydrogen (48) is also fed to this reactor, where the hydrogen reacts with the acetophenone to form α-methyl benzyl alcohol (49). The vent gas streams from this reactor are labeled A_{17} and A_{18}. Spent catalyst (K_{12}) is periodically removed from the reactor and replaced with fresh catalyst. The crude α-methyl benzyl alcohol (49) from this reactor is held in the crude α-MBA receiver tank and then recycled to the α-MBA—AP intermediate storage tank. A mixed stream of hydrogen and nitrogen (48) is used periodically to activate the catalyst in this hydrogenation reactor.

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8. Letter dated Oct. 5, 1979, from S. W. Fretwell, Oxirane Corp., Houston, TX, to Carl A. Peterson, Jr., IT Enviroscience, Inc.
9. C. A. Peterson, IT Enviroscience, Inc., Trip Report for Visit to Oxirane Chemical Co., Channelview, TX, Oct. 18, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals are photochemically unreactive. However, many photochemically unreactive organic chemicals are of concern and may not be exempt from regulation by EPA under Section 111 and 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. CHLOROHYDRINATION PROCESS

1. Model Plant[1—5]

The model plant for this study on the chlorohydrination process for the manufacture of propylene oxide has a production capacity of 68 Gg/yr based on 8760-hr/yr operation.* Actual capacities of newer production plants using this process range up to 454 Gg/yr, but these larger plants are composed of multiple train units, with some larger sized purification systems. Therefore it is presumed that the selected size of the model plant will be somewhat representative of a single train in the multiple-train plants. The flow diagram of the model plant shown in Fig. III-2 is believed to be typical of today's manufacturing and engineering technology as currently practiced. Modern design methods could probably permit the design of larger sized single-train units, but the technology represented is believed to be close enough to be suitable for emission control studies.

2. Sources and Emissions

Sources and emission rates for the chlorohydrination process for propylene oxide are summarized in Table IV-1; the amounts and compositions of the VOC are intended to represent typical emissions from a well-designed and -operated system.

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*Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

Table IV-1. Total Uncontrolled[a] VOC Emissions from the Model Plant for the Manufacture of Propylene Oxide Using the Chlorohydrination Process (68 Gg/yr)

Emission Source	Stream Designation (Fig.III-2)	VOC Emissions[b]		Vent Gas VOC Composition (wt %)						Non-VOC in Vent Gas (wt %)
		Ratio (g/kg)[c]	Rate (kg/hr)	C_2	C_3	PO	DCP	DCIPE	Other	
Vent gas scrubber vent	A_1	10.25	79.57	5.0	78.4				16.6	4.7
Saponification column vent	A_2	0.043	0.33			90			10	47.0
PO stripping column vent	A_3	0.006	0.05			89.9			10.1	46.2
Lights stripping column vent	A_4	0.006	0.05			79.9			20.1	46.2
PO final distillation column vent	A_5	0.006	0.05			100			Trace	46.2
DCP distillation column vent	A_6	0.0001	0.0008				98		2	83
DCIPE stripping column vent	A_7	0.000004	0.00003					98	2	97
Fugitive		Not estimated								
Storage and handling		Not estimated								
Secondary		Not estimated								
		10.31	80.05							

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[a] Uncontrolled emissions are emissions from the process for which no specific emission control devices (other than those necessary for economy or safety) have been installed.

[b] VOC emissions exclude methane but include higher-molecular-weight organic compounds such as ethylene, propane, propylene, etc.

[c] g of emission per kg of propylene oxide produced.

a. Vent Gas Scrubber Vent——This vent (A_1, Fig. III-2) discharges the vent gas from the chlorohydrin reactors after the gas is scrubbed to remove residual vapors of chlorine and hydrochloric acid. This vent stream is the main emission source from the chlorohydrination process. The source of this vent gas is the inert propane contained in the propylene fed to the chlorohydrin reactors. The propane does not react in the chlorohydrin reactors and exits the system through the vent gas scrubber. This unreactive propane acts as a sweep gas, carrying other vapors and gases with it. The amount and composition given in Table IV-1 are intended to represent typical emissions from a well-designed and -operated process when chemical-grade propylene at a normal purity level is used as feed for the process.

b. Saponification Column Vent——This vent (A_2, Fig. III-2) discharges the inert gases carried into the saponification column along with the column feed streams. The inert gases act as a sweep gas to carry vapors of propylene oxide and other materials along with them as they exit the system. The propylene oxide (PO) from the saponification column is compressed and condensed to yield crude PO. The inert gases that enter the system sweep with the PO through the compressor and condenser and must eventually exit this system through a pressure control valve. They are saturated with propylene oxide vapor from the liquefied PO and carry the vapor with the inert gases as they exit.

c. PO Stripping Column Vent——This vent (A_3, Fig. III-2) discharges the inert gases carried into the PO stripping column along with the column feed streams. The inert gases act as sweep gases to carry vapors of propylene oxide and other materials along with them as they exit the system.

d. Lights Stripping Column Vent——This vent (A_4, Fig. III-2) discharges the inert gases carried into the lights stripping column along with the column feed stream. The inert gases act as sweep gases to carry with them vapors of propylene oxide and other materials as they exit the system.

e. PO Final Distillation Column Vent——This vent (A_5, Fig. III-2) discharges the inert gases carried into the PO final distillation column along with the column feed stream. The inert gases act as sweep gases and carry vapors of propylene oxide and other materials along with them as they exit the system.

f. DCP Distillation Column Vent——This vent (A_6, Fig. III-2) discharges the inert gases carried into the DCP (dichloropropane) distillation column along with the column feed stream. The inert gases act as sweep gases to carry with them vapors of DCP and other materials as they exit the system.

g. DCIPE Distillation Column Vent——This vent (A_7, Fig. III-2) discharges the inert gases carried into the DCIPE (dichloroisopropyl ether) distillation column along with the column feed stream. The inert gases act as sweep gases to carry with them vapors of DCIPE and other materials as they exit the system.

h. Fugitive Emissions——Process pumps, piping flanges, compressor shaft seals, and valves are all potential sources of fugitive emissions. No attempt has been made to estimate the total number of pumps, flanges, compressors, valves, or their emission characteristics for this model plant. Refer to the separate fugitive emissions report[6] for additional information on this subject.

i. Storage and Handling Emissions——Emissions result from the storage and handling of raw materials, intermediates, finished products, by-products, and waste streams. No attempt has been made to estimate quantity, size, condition, or emissions generated by the storage requirements or handling requirements of this model plant. Refer to the separate storage and handling report[7] for additional information on this subject.

j. Secondary Emissions——The principal sources of secondary VOC emissions are the process waste streams generated by this process. No attempt has been made to estimate the secondary emissions generated by the storage, handling, processing, or treatment of the various waste streams generated by this process. Refer to the separate secondary emissions report[8] for additional information on this subject.

B. ISOBUTANE HYDROPEROXIDE PROCESS

1. Model Plant[1—4,9,10]

The model plant for this study on the isobutane hydroperoxide process for the manufacture of propylene oxide has a production capacity of 417 Gg/yr based on 8760-hr/yr operation. This selected capacity is a close match to the current nominal production capacity of the Oxirane Bayport plant, the only domestic plant manufacturing propylene oxide by this process. It is recognized that some sections of this plant consist of multitrain units, but this type of construction is not expected to cause significant variations in the emission calculations used for the model plant. It is believed that the flow diagram of the model plant shown in Fig. III-4 is typical of today's manufacturing and engineering technology.

2. Sources and Emissions

Sources and emission rates for the isobutane hydroperoxide process for propylene oxide are summarized in Table IV-2; the amounts and compositions of VOC are intended to represent typical emissions from a well-designed and -operated plant.

a. Oxidation Reactor Scrubber Vent——This vent (A_1, Fig. III-4) discharges the inert gases carried into the oxidation reactors with the purified oxygen. These inert gases are saturated with organic vapors and act as a sweep gas to carry the VOC out of the reactors. A caustic scrubber is used to remove carbonyl compounds from the inert gas stream. Another scrubber, containing cool t-butyl alcohol (TPA), is used to absorb and remove organic vapors (principally isobutane) from this vent gas stream before the vent gas is discharged. The TBA scrubber is required to reduce the concentration of isobutane in the vent gas to economically acceptable levels.[9]

b. TBA Stripping Column Vent——This vent (A_2, Fig. III-4) discharges the inert gases carried into the TBA stripping column with the column feed streams. The inert gases act as sweep gases to carry with them TBA vapors and other materials as they exit the system.

c. Catalyst Mix Tank Vent——Fluctions in tank liquid level and temperature result in the inert gases that enter the tank being discharged through the opening of this vent (A_3, Fig. III-4). These inert gases are saturated with propylene glycol vapor and act as a sweep gas to carry this VOC out of the tank vent.

d. PO Stripping Column Vent——This vent (A_4, Fig. III-4) discharges the inert gases that enter this column with the feed stream. These inert gases are saturated with propylene oxide vapor and act as a sweep gas to carry this VOC out of the column vent.

Table IV-2. Total Uncontrolled VOC Emissions from the Model Plant for the Manufacture of Propylene Oxide Using the Isobutane Hydroperoxide Process (417 Gg/yr)

Emission Source	Stream Designation (Fig.III-4)	VOC Emissions[b]		Vent Gas VOC Composition (wt%)										Non-VOC in Vent Gas (wt %)
		Ratio (g/kg)[c]	Rate (kg/hr)	Methanol	C_2	C_3	C_4	TBA	PO	PG	Acetone	Solvent	Other	
Oxidation reactor scrubber vent	A_1	1.76	83.8		Trace	Trace	49	51					Trace	78
TBA stripping column vent	A_2	0.004	0.19					100					Trace	73
Catalyst mix tank vent	A_3	0.000012	0.0006							100			Trace	99
PO stripping column vent	A_4	0.0185	0.88					Trace	100				Trace	58
Crude TBA recovery column vent	A_5	0.0155	0.74					100	Trace				Trace	57
TBA wash-decant system vent	A_6	0.00714	0.34		Trace	Trace	85	15					Trace	65
Wastewater stripping column vent	A_7	0.95	45.2		Trace	Trace	78	7			13		2	2.8
Solvent scrubber vent[d]	A_8	0.63	30.0						0.5			99.5	Trace	94
Solvent recovery column vent	A_9	0.00046	0.02									100	Trace	85
Water stripping column vent	A_{10}	0.0013	0.06	20						Trace	80		Trace	20
Propylene glycol column and dipropylene glycol column combined vent	A_{11}	0.058	2.76							100			Trace	96
Wastewater stripping column vent	A_{12}	1.33	63.3	5.8			29.7				64.5		Trace	0.3
Plant furnace flue gas vents	A_{13}	0.040	1.90										100	99.9+
Fugitive		Not estimated												
Storage and handling		Not estimated												
Secondary		Not estimated												
		4.81	229.17											

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[a] Uncontrolled emissions are emissions from the process for which no specific emission control devices (other than those necessary for economy or safety) have been installed.

[b] VOC emissions exclude methane, but include higher-molecular-weight organic compounds such as ethane, ethylene, propane, propylene, etc.

[c] g of emission per kg of propylene oxide produced.

[d] See ref 10.

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e. Crude TBA Recovery Column Vent——This vent (A_5, Fig. III-4) discharges the inert gases that enter this column with the feed stream or by internal column pressure fluctuations. These inert gases are saturated with t-butyl alcohol vapor and act as a sweep gas to carry this VOC out of the column vent.

f. TBA Wash-Decant System Vent——This vent (A_6, Fig. III-4) discharges the inert gases that enter this system with the system feed streams and/or the pad-gas manifold. These inert gases are saturated with isobutane and t-butyl alcohol vapor and act as a sweep gas to carry these VOC out of the system vent.

g. Wastewater Stripping Column Vent——This vent (A_7, Fig. III-4) discharges the inert gases that enter this column with the feed stream or by internal column pressure fluctuations. These inert gases are saturated with isobutylene and t-butyl alcohol vapors and act as a sweep gas to carry these VOC vapors out of the column vent.

h. Solvent Scrubber Vent——This vent (A_8, Fig. III-4) discharges the vent gases from the various PO feed and storage tanks and the vent gases from the solvent-PO separation column and the PO finishing column after all these vent gases are scrubbed with solvent to absorb and remove most of the propylene oxide contained in the vent gases. The vent gas exiting the scrubber is saturated with equilibrium concentrations of solvent vapor and residual propylene oxide.[9]

i. Solvent Recovery Column Vent——This vent (A_9, Fig. III-4) discharges the inert gases that enter the column with the feed stream or by internal column pressure fluctuations. These inert gases are saturated with solvent vapor and act as a sweep gas to carry this VOC out of the column vent.

j. Water Stripping Column Vent——This vent (A_{10}, Fig. III-4) discharges the inert gases that enter the column with the column feed stream or by internal column pressure fluctuations. These inert gases are saturated with water vapor, residual carbonyl materials (acetone, etc.), and a trace of propylene glycol vapor and act as a sweep gas to carry these VOC vapors out of the column vent.

k. Propylene Glycol Column and Dipropylene Glycol Column Combined Vent——This vent (A_{11}, Fig. III-4) discharges the inert gases that enter the columns with the column feed streams or by internal column pressure fluctuations. These inert gases are saturated with vapors of propylene glycol and dipropylene glycol and act as a sweep gas to carry these VOC vapors out of the column vents.

l. Wastewater Stripping Column Vent——This vent (A_{12}, Fig. III-4) discharges the inert gases that enter the column with the column feed streams or by internal column pressure fluctuations. These inert gases are saturated with vapors of carbonyl compounds (acetone, methanol, etc.), along with some hydrocarbon vapor and water vapor from the VOC being stripped out of the wastewater. These inert gases act as a sweep gas to carry these VOC vapors out of the column vent.

m. Process Furnace Flue Gas Vents——These vents (A_{13}, Fig. III-4) represent the discharge of flue gas combustion products from the process furnaces used in the model plant to burn the fuel-rich waste streams from the process for process heating requirements. These flue gases contain traces of aldehydes from combustion of the various hydrocarbons in the fuel-rich waste streams.[11]

n. Fugitive Emissions——Process pumps, piping flanges, compressor shaft seals, and valves are all potential sources of fugitive emissions. No attempt has been made to estimate the total number of pumps, flanges, compressors, valves, or their emissions characteristics for this model plant. Refer to the separate fugitive emissions report[6] for additional information on this subject.

o. Storage and Handling Emissions——Emissions result from the storage and handling of raw materials, intermediates, finished products, by-products, and waste streams. No attempt has been made to estimate quantity, size, condition, or emissions generated by these various storage and handling requirements of this model plant. Refer to the separate storage and handling report[7] for additional information on this subject.

p. Secondary Emissions——The principal sources for secondary emissions are the waste streams generated by the process. No attempt has been made to estimate the secondary emissions generated by the storage, handling, processing, or treatment of the various waste streams generated by the model plant. Refer to the separate secondary emissions report[8] for additional information on this subject.

C. ETHYLBENZENE HYDROPEROXIDE PROCESS

1. Model Plant[1—4,12]

The model plant for this study on the ethylbenzene hydroperoxide process for the manufacture of propylene oxide has a production capacity of 181 Gg/yr based on 8760-hr/yr operation. This selected capacity is a close match to the current nominal production capacity of the Oxirane Channelview plant, the only domestic plant manufacturing propylene oxide by this process. It is recognized that some sections of the plant consist of multitrain units but this type of construction is not expected to cause significant variations in emission calculations used for the model plant. It is believed that the flow diagram of the model plant shown in Fig. III-6 is typical of today's manufacturing and engineering technology.

2. Sources and Emissions

Sources and emission rates for the ethylbenzene hydroperoxide process for propylene oxide are summarized in Table IV-3; the amounts and compositions of VOC are intended to represent typical emissions from a well-designed and -operated plant.

a. Oxidation Reactor Scrubber Vent——This vent (A_1, Fig. III-6) discharges the inert gases carried into the oxidation reactor with the compressed air used for oxidation of the ethylbenzene. This stream of oxygen-depleted air is saturated with vapors of ethylbenzene and other VOC. These gases are scrubbed with oil (α-methyl benzyl alcohol—acetophenone, α-MBA—AP) and water for recovery of most of the hydrocarbon vapors swept out of the reactor system by the inert gases. The vent gas scrubbers could be considered emission control devices, but for purposes of this report they are classified as a necessary part of the process to reduce ethylbenzene vapor losses to economically acceptable levels.

b. FF Evaporator Vent——This vent (A_2, Fig. III-6) discharges the inert gases carried into the falling film evaporator with the evaporator feed stream. These inert gases are saturated with ethylbenzene vapor and act as a sweep gas to carry the VOC vapors with them as they exit the system.

Table IV-3. Total Uncontrolled VOC Emissions from the Model Plant for the Manufacture of Propylene Oxide Using the Ethylbenzene Hydroperoxide Process (181 Gg/yr)

Emission Source	Stream Designation (Fig. III-6)	VOC Emissions[b]		Vent Gas VOC Composition (wt %)						Non-VOC in Vent Gas (wt %)
		Ratio (g/kg)[c]	Rate (kg/hr)	C_2	C_3	PO	EB	Styrene	Other	
Oxidation reactor scrubber vent[d]	A_1	1.61	33.5				50		50	99.9+
FF evaporator vent	A_2	0.0051	0.11				95		5	90
Catalyst mix tank vent	A_3	Trace	Trace				95		5	~100
Separation column vent	A_4	0.16	3.31	5	95				Trace	17
Lights stripping column vent	A_5	0.16	3.31	20	80				Trace	17
Propylene recovery column vent	A_6	0.16	3.31		100				Trace	17
Product wash-decant system vent	A_7	0.0005	0.01			95			5	88
Mixed HC wash-decant system vent	A_8	0.0015	0.03				98		2	90
EB wash-decant system vent	A_9	0.0014	0.03				100		Trace	90
EB stripping column vent	A_{10}	0.0015	0.03				98		2	90
Light HC stripping column vent	A_{11}	0.0015	0.03				95		5	90
α MBA-AP stripping column vent	A_{12}	0.0080	0.17						100	99+
Catalyst mix tank vent	A_{13}	Trace	Trace						100	~100
Dehydration reactor system vent	A_{14}	0.0008	0.02				5	95	Trace	99+
Light impurities stripping column vent	A_{15}	1.24	25.7				95	2	3	90
Styrene finishing column vent	A_{16}	0.83	17.2				Trace	100	Trace	90
Hydrogenation reactor operating vent	A_{17}	Normally 0	Normally 0							
Hydrogenation reactor activation vent	A_{18}	Normally 0	Normally 0							
Fugitive		Not estimated								100
Storage and handling		Not estimated								
Secondary		Not estimated								
		4.18	86.6							

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[a] Uncontrolled emissions are emissions from the process for which no specific emission control devices (other than those necessary for economy or safety have been installed.

[b] VOC emissions exclude methane, but include higher-molecular-weight organic compounds such as ethane, ethylene, propane, propylene, etc.

[c] g of emission per kg of propylene oxide produced.

[d] See ref 12.

c. Catalyst Mix Tank Vent—This vent (A_3, Fig. III-6) discharges the inert gases that enter the catalyst mix tank because of fluctuations in liquid level and temperature in the tank. These gases are saturated with VOC vapors, which are swept out as the gases exit the tank vent. Due to low vapor pressure and small flows of inert gases, the amount of VOC in this vent stream is very low.

d. Separation Column Vent—This vent (A_4, Fig. III-6) discharges the inert gases that enter the Separation Column with the column feed streams. These inert gases are saturated with propylene vapor and, acting as a sweep gas, carry the VOC vapor with them as they exit the column.

e. Lights Stripping Column Vent—This vent (A_5, Fig. III-6) discharges the inert gases that enter the lights stripping column with the column feed stream. These inert gases are saturated with a mixture of low-boiling-point hydrocarbon vapors, which are swept out with the gases as they exit the column.

f. Propylene Recovery Column Vent—This vent (A_6, Fig. III-6) discharges the inert gases that enter the propylene recovery column with the column feedstream. These inert gases, which are saturated with propylene vapor, sweep the VOC vapors with them as they exit the column.

g. Product Wash-Decant System Vent—This vent (A_7, Fig. III-6) discharges the inert gases that enter the system with the system feed streams. These inert gases are saturated with propylene oxide vapor and other VOC vapors, which are swept out with the gases as they exit the wash-decant system.

h. Mixed HC Wash-Decant System Vent—This vent (A_8, Fig. III-6) discharges the inert gases that enter the system with the system feed streams. These inert gases are saturated with vapors of ethylbenzene and other VOC. The inert gases sweep these vapors with them as they exit the system.

i. EB Wash-Decant System Vent—This vent (A_9, Fig. III-6) discharges the inert gases that enter the system with the system feed streams. These gases are saturated with vapors of ethylbenzene, which are swept out of the system by the inert gases as they exit the system.

j. EB Stripping Column Vent—The inert gases that enter the column with the column feed streams are discharged from this vent (A_{10}, Fig. III-6) and are saturated with vapors of ethylbenzene and other VOC. These vapors are swept out of the column along with the exiting inert gases.

k. Light HC Stripping Column Vent—This vent (A_{11}, Fig. III-6) discharges the inert gases that enter the column with the column feed stream. These inert gases are saturated with mixed hydrocarbon vapors, and sweep these vapors with them as they exit the column.

l. α-MBA—AP Stripping Column Vent—This vent (A_{12}, Fig. III-6) discharges the inert gases that bleed into this vacuum distillation column through the leaks in the column system assembly. When discharged from the atmospheric exhaust of the vacuum steam-jet system, these inert gases are saturated with water vapor and VOC vapors.

m. Catalyst Mix Tank Vent—This vent (A_{13}, Fig. III-6) discharges the inert gases that enter the catalyst mix tank because of fluctuations in liquid level and temperature in the tank. These gases are saturated with vapors of VOC from the tank liquid, and sweep the VOC vapors out of the tank vent. Due to low vapor pressure and small flows of inert gases, the amount of VOC in this vent stream is very low.

n. Dehydration Reactor System Vent—This vent (A_{14}, Fig. III-6) discharges the inert gases that enter the system with the system feed stream. These inert gases are saturated with vapors of mixed VOC, which are swept out with the inert gases as they exit the system.

o. Light Impurities Stripping Column Vent—This vent (A_{15}, Fig. III-6) discharges the inert gases that bleed into this vacuum distillation column through the leaks in the column system assembly. When the inert gases are discharged from the atmospheric exhaust of the vacuum steam jet system, they are saturated with water vapor and VOC vapor.

p. Styrene Finishing Column Vent—This vent (A_{16}, Fig. III-6) discharges the inert gases that bleed into this vacuum distillation column through the leaks in the column system assembly. When the inert gases are discharged from the atmospheric exhaust of the vacuum steam-jet system, they are saturated with water vapor and styrene monomer vapor.

q. Hydrogenation System Operating Vent——This vent (A_{17}, Fig. III-6) does not normally open and discharge any inert gases or VOC vapors. The small amount of inert gases that enter the system with the feed streams normally dissolve in the liquid and exit the reactor with the product stream.

r. Hydrogenation System Activation Vent——This vent (A_{18}, Fig. III-6) discharges a mixture of hydrogen and nitrogen when a feed stream of mixed hydrogen and nitrogen is used to periodically activate the reactor catalyst. Since all organic materials are removed prior to activation, this vent stream normally does not contain any VOC vapors.

s. Fugitive Emissions——Process pumps, piping flanges, compressor shaft seals, and valves are all potential sources of fugitive emissions. No attempt has been made to estimate the total number of pumps, flanges, compressors, valves, or their emission characteristics for this model plant. Refer to the Fugitive Emissions report[6] for additional information on this subject.

t. Storage and Handling Emissions——Emissions result from the storage and handling of raw materials, intermediates, finished products, by-products, and waste streams. No attempt has been made to estimate quantity, size, condition, or emissions generated by the various storage and handling requirements of this model plant. Refer to the Storage and Handling report[7] for additional information on this subject.

u. Secondary Emissions——The principal sources for secondary emissions are the waste streams generated by the process. No attempt has been made to estimate the secondary emissions generated by the storage, handling, processing, or treatment of the various waste streams generated by the model plant. Refer to the Secondary Emissions report[8] for additional information on this subject.

D. OTHER PROCESSES[1—4]

The literature describes other processes for the manufacture of propylene oxide, but the three processes previously described are the only ones now practiced domestically. The electrochemical version of the chlorohydrination process is being promoted by Lummus,[13] but emission characteristics and process economics for this approach are expected to be similar to those of the original clorohydrination process.

In the hydroperoxide process it is possible to substitute other easily oxidized hydrocarbons for isobutane or ethylbenzene (cumene, for example). When such a substitution is made, the propylene—propylene oxide conversion is essentially unchanged, but the conversion of the hydrocarbon to hydroperoxide to alcohol yields a different coproduct, depending on the starting material. For the hydroperoxide process to be economical, the coproduct alcohol must either be a valuable product or be convertible to a valuable product. An alternative on convertability includes the possibility of converting the alcohol coproduct back to the starting hydrocarbon for recycle. If other hydroperoxide processes are adopted for domestic use, their emission characteristics are expected to be similar to those of the two existing hydroperoxide processes.

A third alternative route to the manufacture of propylene oxide is the direct oxidation of propylene with either air or purified oxygen in a manner similar to the present processes for ethylene oxide. A lot of research has been performed in various attempts to find catalysts and process conditions economically favorable for this direct oxidation route to propylene oxide, but published results to date indicate poor yields and/or conversion rates. If future research on an economically competitive direct oxidation route is successful, the emission characteristics of this process are expected to be similar to those of one of the two existing versions of the ethylene oxide direct oxidation process.

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V. APPLICABLE CONTROL SYSTEMS

A. CHLOROHYDRINATION PROCESS[1]

Table V-1 contains a tabulation of controlled emissions from the chlorohydrin process model plant. These control techniques are discussed as follows:

1. Vent Gas Scrubber Vent

This stream (A_1, Fig. III-2) from the vent gas scrubber vent is the largest and most significant source of VOC emissions for the model plant and consists principally of propane with some residual unreacted propylene. Also present in this vent gas stream are water vapor and small amounts of hydrochloric acid and chlorine. Because of these non-VOC contaminants this vent gas is corrosive and difficult to handle. Its heating value is approximately 3.8 GJ/hr for the model plant.

The source of the residual propane that is the principal cause of the VOC emission is the unreactive propane that enters the system with the chemical-grade propylene used to manufacture propylene oxide. Chemical-grade propylene contains up to 5% propane and other nonreactive hydrocarbons. Another source of nonreactive inert gases in this vent are those that enter the system with the chlorine used to hydrochlorinate the propylene. These inert gases are not a direct source of VOC, but they function as a sweep gas to carry VOC out of the reactor system.

Several alternatives for reduction of VOC emissions from this source are possible, as described below:

(a) Upgrade the purity of the propylene used in this process by switching to polymer-grade propylene instead of chemical-grade propylene. This switch in propylene purity levels would reduce the VOC emissions by at least 70% by reducing the amount of nonreactive propane entering the system. This technique is recommended by Dow[1] as the most cost-effective method for reduction of the major VOC emissions from this process.

(b) Upgrade the purity of the chlorine used in this process to the purity level of liquid chlorine (about 99.5%) from the lower quality level of in-plant gaseous chlorine containing a significantly higher level of nonreactive

Table V-1. VOC Controlled Emissions for Model Plant Producing Propylene Oxide by the Chlorohydrination Process (68 Gg/yr)[a]

Emission Source	Stream Designation (Fig.III-2)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Controlled Emissions	
				Ratio (g/kg)[b]	Rate (kg/hr)
Vent gas scrubber vent	A_1	Upgrade purity of propylene feedstock	70	3.07	23.87
Saponification column vent	A_2	Fume water scrubber	95	0.0021	0.017
PO stripping column vent	A_3	Fume water scrubber	95	0.0003	0.0025
Lights stripping column vent	A_4	Fume water scrubber	95	0.0003	0.0025
PO final distillation column vent	A_5	Fume water scrubber	95	0.0003	0.0025
DCP distillation column vent	A_6	Fume oil scrubber	90	0.00001	0.00008
DCIPE stripping column vent	A_7	None	0	0.000004	0.00003
Fugitive				Not estimated	
Storage and handling				Not estimated	
Secondary				Not estimated	
				3.078	23.90

[a] See ref 1.

[b] g of emission per kg of propylene oxide produced.

inerts. This technique would not reduce the emissions of nonreactive propane contained in the propylene feedstock, but by reducing the quantity of inert sweep gas, could reduce the amount of propylene swept out of the system. Emission reduction might be in the range of 20 to 50% if this control technique were adopted. This method could be combined with the technique described in (a) for an overall reduction in emissions of up to 85%.

(c) Destroy the VOC contained in the vent gas by feeding this vent gas through a thermal incinerator (or flare) to convert the hydrocarbons to carbon dioxide and water vapor. This incineration approach would be expected to destroy 95 to 99% of the contained VOC, depending on the efficiency of the combustion process used. The presence of small amounts of chlorine and hydrochloric acid vapor in the vent gas would require the use of corrosion-resistant construction for the ductwork and thermal oxidizer used to handle the gas.

(d) Install an oil scrubber system and associated hydrocarbon stripping column to scrub the propane and associated hydrocarbons out of this vent stream and to recover the propane, etc., from the stripping column for use as a fuel. This technique could remove up to 95% of the VOC from the vent gas stream for recovery as a fuel. Because of the corrosive nature of this vent gas, at least the scrubber and its associated ductwork would have to be fabricated of corrosion-resistant materials. The presence of chlorine in the vent gas would require extra care in the selection of a scrubber fluid to avoid absorption of and reaction with chlorine. A design approach that is used to reduce the problems caused by the presence of chlorine and hydrochloric acid in this vent gas is the installation of an alkali scrubber (dilute caustic scrubber) to pretreat the gas stream before treating the vent gas in an oil scrubber to remove the contained VOC.

2. Saponification Column Vent

The stream from the vent (A_2, Fig. III-2) on the saponification column is small and is rich in propylene oxide (PO). This vent gas can be sent to a water scrubber, where the propylene oxide would be absorbed and eventually converted to a dilute aqueous solution of propylene glycol. It is not necessary to provide one dedicated water scrubber for each vent containing PO, since one larger sized scrubber can accommodate as many vent streams as can be conveniently piped to the scrubber location. With a properly designed scrubber, a PO removal efficiency of 95% or better can reasonably be achieved.

3. PO Stripping Column Vent
The stream from the vent (A_3, Fig. III-2) on the PO stripping column is a small vent stream rich in propylene oxide. This vent stream can be treated by using a water scrubber, as described in V-A-2.

4. Lights Stripping Column Vent
The stream from the vent (A_4, Fig. III-2) on the lights stripping column is a small stream rich in propylene oxide. This vent stream can be treated by using a water scrubber, as described in V-A-2.

5. PO Final Distillation Column Vent
The stream from the vent (A_5, Fig. III-2) on the PO final distillation column is small and is rich in propylene oxide. This vent stream can also be treated by using a water scrubber, as described in V-A-2.

6. DCP Distillation Column Vent
The stream from the vent (A_6, Fig. III-2) on the DCP distillation column is a small one containing a very small quantity of dichloropropane. It is possible to remove most of the dichloropropane from this vent gas stream either by the use of an "oil" scrubber or by adsorption of the DCP on activated charcoal in an adsorption canister. Either regeneration of the absorption or adsorption medium would be required or the absorbent or adsorbent would need periodic replacement. Absorption or adsorption can achieve 90% or better removal of the DCP from the vent gas, but because of the small amount of VOC in this stream, the cost/benefit ratio for removal is expected to be relatively high.

7. DCIPE Stripping Column Vent
The stream from the vent (A_7, Fig. III-2) on the DCIPE stripping column is small and contains an extremely small amount of dichloroisopropyl ether. It is possible to remove a large part of this DCIPE from the vent gas by the use of either an "oil" scrubber or a canister of activated charcoal. Because of the low concentration of DCIPE in the vent gas, the removal efficiency by either technique is

expected to be probably 80% or lower. Because of the small quantity of VOC in this vent stream, it is expected that the cost/benefit ratio for removal would be extremely high.

B. ISOBUTANE HYDROPEROXIDE PROCESS[2]

Table V-2 gives the controlled emissions from the isobutane hydroperoxide process model plant. The techniques for controlling these emissions are discussed as follows:

1. Oxidation Reactor Scrubber Vent

The stream from the oxidation reactor scrubber vent (A_1, Fig. III-4) is the largest and most significant source of VOC emissions for the model plant and consists principally of isobutane and t-butyl alcohol (TBA) vapors in an inert gas stream. The caustic scrubber and the TBA vent scrubber have reduced the VOC levels to economically acceptable loss levels, but it is possible to reduce this residual VOC further by VOC emission control techniques. Some possible alternative techniques for VOC emission reduction are as follows:

(a) Replace the TBA vent scrubber with a lean-oil absorber and regeneration system. Use of this technique, whereby a low-vapor-pressure oil is used in place of TBA as the scrubbing fluid, would eliminate the TBA vapors from the vent gas while still permitting the isobutane to be recovered from the vent gas stream. Emission reduction would be at least 50% with this approach.

(b) Install an activated-carbon adsorption system after the TBA vent scrubber to remove and recover most of the VOC in the vent stream. Depending on the design and operating conditions for this adsorption-desorption-recovery system, the VOC emission reduction might lie in the range of 60 to 85%.

(c) Collect the vent gas stream and send it to a thermal destruction device (fume incinerator or flare) for oxidation of the contained VOC. Most fume incinerators operate at 99% efficiency, or better, and most flares operate in an efficiency range of 98% or better*.

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*Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies cited are for tentative comparison purposes.

Table V-2. Controlled Emissions for Model Plant Producing Propylene Oxide by the Isobutane Hydroperoxide Process (417 Gg/yr)[a]

Emission Source	Stream Designation (Fig.III-4)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Controlled Emissions Ratio (g/kg)[b]	VOC Controlled Emissions Rate (kg/hr)
Oxidation reactor scrubber vent	A_1	Plant flare	98	0.0352	1.676
TBA stripping column vent	A_2	Vent condenser	60	0.0014	0.144
Catalyst mix tank vent	A_3	None		0.000012	0.0006
PO stripping column vent	A_4	Fume water scrubber	95	0.00093	0.044
Crude TBA recovery column vent	A_5	Fume water scrubber	95	0.00078	0.037
TBA wash-decant system vent	A_6	Plant flare	98	0.00036	0.007
Wastewater stripping column vent	A_7	Vent condenser	80	0.190	9.04
Solvent scrubber vent	A_8	Plant flare	98	0.013	0.6
Solvent recovery column vent	A_9	Plant flare	98	0.0000	0.0004
Water stripping column vent	A_{10}	Plant flare	98	0.00002	0.0012
Propylene glycol column and dipropylene glycol column combined vent	A_{11}	Fume water scrubber	95	0.0029	0.138
Wastewater stripping column vent	A_{12}	Vent condenser	80	0.266	12.66
Plant furnace flue gas vents	A_{13}	None		0.040	1.90
Fugitive				Not estimated	
Storage and handling				Not estimated	
Secondary				Not estimated	
				0.551	26.25

[a] See ref 2.

[b] g of emission per kg of propylene oxide product.

2. TBA Stripping Column Vent

The stream from the vent (A_2, Fig. III-4) on the TBA stripping column is a small one rich in TBA vapor. The most likely technique for reduction of VOC emission from this source would be the installation of a refrigerated vent condenser on the vent line prior to the column pressure control valve. Depending on design and operating conditions a vent condenser might recover 60 to 90% of the contained VOC. Because of the small quantity of VOC in the vent, it is expected that the cost-benefit ratio would be relatively high for any device used to reduce VOC emissions from this source.

3. Catalyst Mix Tank Vent

The vent gas stream (A_3, Fig. III-4) from the catalyst mix tank contains an extremely small quantity of propylene glycol as the principal VOC. Because of the minute amount of VOC emitted by this vent, no emission control technique is specified.

4. PO Stripping Column Vent

The stream from the vent (A_4, Fig. III-4) on the PO stripping column is small and is rich in propylene oxide. This vent gas can be sent to a water scrubber, where the propylene oxide would be absorbed and eventually converted to a dilute aqueous solution of propylene glycol. It is not necessary to provide one dedicated water scrubber for each vent containing PO, since one larger sized scrubber can accommodate as many vent streams as can be conveniently piped to the scrubber location. With a properly designed scrubber, a PO removal efficiency of 95% or better can reasonably be achieved.

5. Crude TBA Recovery Column Vent

The stream from the vent (A_5, Fig. III-4) on the crude TBA recovery column is small and is rich in TBA vapor. A possible recovery technique for this VOC would be the installation of a refrigerated vent condenser on the vent gas line before the column relief valve. Such a condenser could recover 60 to 90% of the contained VOC, depending on column operating pressure and vent condenser design. Because of the small size of this vent stream, cost-benefit ratios for VOC reduction of this technique would be relatively high. An alternative approach for control of this VOC would be to direct the vent gas stream to the same water scrubber used to absorb PO, as described in V-B-4.

6. TBA Wash-Decant System Vent

The vent gas stream (A_6, Fig. III-4) from the TBA wash-decant system is very small and is rich in isobutane, with some TBA. Because of the small size of this vent stream, techniques that would be suitable for larger streams, such as a lean-oil absorption-recovery system or an activated-carbon adsorption-recovery system, probably would not have an acceptable cost-benefit ratio. The system of choice would be to pipe the vent gas to a common vent header leading to a thermal oxidation system sized to handle multiple vent gas streams (such as a vent gas incinerator or flare), as described in V-B-1-(c). Flare efficiency is estimated to be 98%.

7. Wastewater Stripping Column Vent

The vent gas stream (A_7, Fig. III-4) on the wastewater stripping column is a fairly large stream rich in isobutylene and also contains some other organic materials, such as acetone and TBA. The most likely technique for reduction of VOC emissions from this source would be the installation of a refrigerated vent condenser in the column vent line before the column relief valve. Depending on column operating pressure and vent condenser design this recovery technique might remove from 80 to 95% of the VOC. An alternative technique would be to pipe the vent stream to a common vent header leading to a thermal oxidizer system (vent gas incinerator or flare), as described in V-B-1-(c).

8. Solvent Scrubber Vent

The stream from the vent (A_8, Fig. III-4) on the solvent scrubber contains an extremely small amount of VOC, principally vapors of solvent. This scrubber is used to recover propylene oxide vapors from the vents on the various propylene oxide distillation columns and associated receivers and tanks. The scrubber could possibly be classified as an emission control device in its own right, but it is present in the model plant as an economically justified yield improvement system. The amount of VOC in this vent stream is so small that cost-benefit ratios would be extremely high for any effective emission control device. The only possibility that would even approach reasonable cost effectiveness would be to pipe the vent gas to a common vent header leading to a thermal oxidizer system, as described in V-B-1-(c). Even this approach would be expensive for the VOC emission reduction that could be achieved. Flare efficiency is estimated at 95% for this small stream in a multiuse flare.

9. Solvent Recovery Column Vent

The vent gas stream (A_9, Fig. III-4) on the solvent recovery column contains an extremely small amount of VOC, principally vapors of solvent. Since the amount of VOC in this vent stream is so small, cost-benefit ratios would be extremely high for any effective emission control device. Connecting this vent to the vent header going to the solvent scrubber would reduce overall VOC emissions from this source by approximately 40%. The most reasonable cost-effective technique would be to pipe the vent stream to a vent header leading to a thermal oxidizer system, as described in V-B-1-(c). Even this approach would be expensive for the VOC emission reduction that could be achieved. Flare efficiency is estimated at 98%.

10. Water Stripping Column Vent

The stream from the vent (A_{10}, Fig. III-4) on the water stripping column contains a very small amount of VOC, principally acetone, which would therefore make cost-benefit ratios very high for any effective emission control device. A refrigerated vent condenser could be installed to reduce VOC emissions, but installation and operating costs would be very high. A more reasonable approach might be to pipe the vent stream to a common vent header leading to a thermal oxidizer system, as described in V-B-1-(c). Even this approach would be expensive for the VOC emission reduction that could be achieved. Flare efficiency is estimated at 98%.

11. Propylene Glycol Column and Dipropylene Glycol Column Combined Vent

This combined vent stream (A_{11}, Fig. III-4) contains a relatively small amount of VOC, principally propylene glycol vapor, thereby making the cost-benefit ratios relatively high for the amount of VOC reduction achieved. The most likely candidate for control of this VOC emission would be a cold-water scrubbing system to absorb the propylene glycol vapors. A well-designed scrubbing system would be expected to remove more than 95% of the VOC from the vent gas. A possible alternative to a separate water scrubber for this vent would be to pipe the vent stream to a combined vent header leading to the water scrubber recommended in V-B-4 if the PO stripping column vent is reasonably close to the combined vent of these glycol distillation columns. In either case it is expected that the cost would be high for the amount of VOC reduction achieved.

12. Wastewater Stripping Column Vent

This vent gas stream (A_{12}, Fig. III-4) from the wastewater stripping column is the second largest source of VOC emissions in the model plant. The principal VOC in this vent gas is acetone, along with significant amounts of isobutane and other organics. The suggested technique for control of this VOC emission source is the installation of a refrigerated vent condenser in the column vent line before the column pressure control (relief) valve. Depending on column operating pressure and vent condenser system design the removal efficiency could vary from 80 to 99+%.

13. Plant Furnace Flue Gas Vents

The flue gas vent stream (A_{13}, Fig. III-4) is a relatively small source of VOC emissions, which are principally aldehydes generated by the combustion process. The fuel used by these plant furnaces is a mixture of various hydrocarbons in gaseous and liquid form. The small quantity of aldehydes generated by combustion of the fuels is present in an extremely low concentration in the flue gases. No effective technique is known for the removal of aldehyde traces from flue gases. The best procedure known for minimizing these emissions is to use properly designed and maintained fuel burners and to use a small amount of excess air above stoichiometric levels for combustion.

C. ETHYLBENZENE HYDROPEROXIDE PROCESS[3]

Table V-3 contains the controlled emissions data for the ethylbenzene hydroperoxide process model plant. The control techniques are discussed as follows:

1. Oxidation Reactor Scrubber Vent

The vent gas stream (A_1, Fig. III-6) from the scrubbers on the oxidation reactors vent is one of the larger VOC emission sources generated by this plant. The principal organic material is ethylbenzene, along with other miscellaneous reaction by-products. The model plant incorporates scrubbers on this emission source to reduce the amount of hydrocarbons and carbonyl compounds in the vent gas. These scrubbers could be considered as emission control devices in their own right, but they are incorporated in the model plant design for safety and economy (material recovery) purposes. The residual VOC in the vent stream is extremely dilute and therefore difficult and expensive to remove. Thermal oxidation is not effective at these low concentration levels. Selective adsorption techniques, such as the use of activated carbon or molecular sieves, are the

Table V-3. VOC Controlled Emissions for Model Plant Producing Propylene Oxide by the Ethylbenzene Hydroperoxide Process (181 Gg/yr)[a]

Emission Source	Stream Designation (Fig.III-6)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Controlled Emissions Ratio (g/kg)[b]	VOC Controlled Emissions Rate (kg/hr)
Oxidation reactor scrubber vent	A_1	Selective adsorption (activated carbon)	80	0.32	6.7
FF evaporator vent	A_2	Plant flare	98	0.000255	0.0055
Catalyst mix tank vent	A_3	None		Trace	Trace
Separation column vent	A_4	Pipe to fuel gas manifold	99	0.0016	0.0331
Lights stripping column vent	A_5	Pipe to fuel gas manifold	99	0.0016	0.0331
Propylene recovery column vent	A_6	Pipe to fuel gas manifold	99	0.0016	0.0331
Product wash-decant system vent	A_7	Fume gas scrubber	95	0.000025	0.0005
Mixed HC wash-decant system vent	A_8	Plant flare	98	0.00003	0.0006
EB wash-decant system vent	A_9	Plant flare	98	0.00003	0.0006
EB stripping column vent	A_{10}	Plant flare	98	0.00003	0.0006
Light HC stripping column vent	A_{11}	Plant flare	98	0.00003	0.0006
α-MBA-AP stripping column vent	A_{12}	Plant flare	98	0.00016	0.0034
Catalyst mix tank vent	A_{13}	None		Trace	Trace
Dehydration reactor system vent	A_{14}	Plant flare	98	0.00002	0.0004
Light impurities stripping column vent	A_{15}	Plant flare	98	0.0248	0.514
Styrene finishing column vent	A_{16}	Plant flare	98	0.0166	0.344
Hydrogenation reactor operating vent	A_{17}	None			
Hydrogenation reactor activation vent	A_{18}	None			
Fugitive				Not estimated	
Storage and handling				Not estimated	
Secondary				Not estimated	
				0.367	7.67

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[a] See ref 3.

[b] g of emission per kg of propylene oxide produced.

only known techniques that can function effectively at these dilution levels. Depending on the adsorbent used and the equipment design, VOC emission reductions of 80 to 95% could be achieved. Because the vent stream is large and has low VOC concentration levels, the cost-benefit ratio for achieving significant emission reduction by adsorption techniques is expected to be relatively high. Activated-carbon adsorption is being piloted by one manufacturer, but results are not yet available.[4]

2. FF Evaporator Vent

The vent stream from the vent (A_2, Fig. III-6) on the FF (falling film) evaporator is relatively small and contains very small amounts of VOC, principally ethylbenzene (EB). Adsorption and recovery techniques could be used to reduce VOC emissions from this source, but the cost-benefit ratio would be extremely high. If a common vent header leading to a thermal oxidation system (fume incinerator or flare) were available to handle multiple vent streams, this small vent stream could be piped to the common vent header as a technique for reducing the VOC emissions. The small quantity of VOC in this vent stream would make the cost-benefit ratio for even that technique relatively high. A flare efficiency of 95% has been assumed.

3. Catalyst Mix Tank Vent

The vent gas stream (A_3, Fig. III-6) from the catalyst mix tank is extremely small and contains only trace levels of VOC, principally ethylbenzene; therefore no emission control technique is suggested to reduce the VOC emissions.

4. Separation Column Vent

The vent gas stream (A_4, Fig. III-6) from the separation column is relatively small but is rich in C_2 and C_3 hydrocarbons. The technique suggested for control of this vent emission is to pipe the vent stream to a common vent header that is used as a fuel gas header to supply process furnaces with gaseous fuel. A discharge pipe from this header could be installed to deliver any excess or unused fuel gas to a thermal oxidizer system (fume incinerator or flare). Thermal combustion of this fuel-rich gas is expected to reduce VOC emissions by at least 99%. Cost-benefit ratios for this control technique are expected to be low (or even negative) since use of the gas as fuel eliminates the need to purchase fuel for heating.

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5. Lights Stripping Column Vent

The gas stream from the vent (A_5, Fig. III-6) on the lights stripping column is similar in size and composition to the vent stream described in V-C-4. The VOC emission control suggestions and comments in V-C-4 apply to this vent stream also.

6. Propylene Recovery Column Vent

This vent stream (A_6, Fig. III-6) from the propylene recovery column is similar in size and composition to the vent stream described in V-C-4. The VOC emission control options described in V-C-4 also apply to this vent stream.

7. Product Wash-Decant System Vent

The stream from the vent (A_7, Fig. III-6) on the product wash-decant system is very small and has propylene oxide as the principal VOC. This vent gas can be sent to a water scrubber, where the propylene oxide would be absorbed and eventually converted to a dilute aqueous solution of propylene glycol. A dedicated water scrubber does not have to be provided for each vent containing PO, since one larger sized scrubber can accommodate as many vent streams as can be conveniently piped to one scrubber location. With a properly designed scrubber a PO removal efficiency of 95% or better can reasonably be achieved. Since this VOC emission source is very small, even piping the vent stream to a nearby water scrubber that is installed to control other PO emission sources is expected to show a very high cost-benefit ratio.

8. Mixed HC Wash-Decant System Vent

Since the stream from the vent (A_8, Fig. III-6) on the mixed HC wash-decant system is a very small one, with ethylbenzene vapor as the principal VOC, the only reasonable VOC emission control technique is to pipe the vent stream to a common vent header leading to a thermal oxidizer system, as described in V-C-2. Because of the small amount of VOC in this vent stream, even the relatively low cost of piping the vent gas to a common vent header is expected to show a very high cost-benefit ratio. A flare efficiency of 98% is assumed.

9. EB Wash-Decant System Vent

The gas stream from the vent (A_9, Fig. III-6) on the EB wash-decant system is similar in size and composition to the vent stream described in V-C-8. The VOC emission control option described in V-C-8 also applies to this vent stream.

10. EB Stripping Column Vent

The EB stripping column vent (A_{10}, Fig. III-6) stream is similar in size and composition to the vent stream described in V-C-8. The VOC emission control option described in V-C-8 also applies to this vent stream.

11. Light HC Stripping Column Vent

The stream from vent A_{11} (Fig. III-6) is similar in size and composition to the vent stream described in V-C-8. Also, the VOC emission control option described in V-C-8 is applicable to this stream.

12. α-MBA-AP Stripping Column Vent

The stream from vent A_{12} (Fig. III-6) on the α-MBA—AP stripping column is significantly larger than the vent stream described in V-C-8 and contains α-methyl benzyl alcohol (α-MBA) as the principal VOC. In spite of this difference this vent stream is still very small, and the option given in V-C-8 on control of VOC emissions also applies to this stream.

13. Catalyst Mix Tank Vent

The stream from the vent (A_{13}, Fig. III-6) on this catalyst mix tank is extremely small and contains only trace levels of VOC, principally α-MBA. No emission control technique is suggested to reduce this extremely low level of VOC emissions.

14. Dehydration Reactor System Vent

The stream from vent A_{14} (Fig. III-6) on the dehydration reactor system is very small and contains styrene monomer as the principal VOC. The VOC emission control option given in V-C-8 applies to this stream also.

15. Light Impurities Stripping Column Vent

The stream from the stripping column vent (A_{15}, Fig. III-6) is the largest vent stream generated by the model plant and contains significant amounts of ethylbenzene and other VOC. The VOC concentration in this vent stream is relatively low, but the total size of the vent stream brings the VOC emissions up to highly significant levels. Several options are available for control of VOC emissions from this source. Some of them are described below:

(a) Use a common vent header to deliver the vent gas to a thermal oxidation system (fume incinerator or flare) for destruction of the VOC. Fume incinerators usually operated at 99% efficiency or better, and flare efficiency is estimated to be 98%. This approach is likely to show the lowest cost-benefit ratio, especially when the possibility of feeding other small vent streams into the common vent header is taken into consideration.

(b) Use a chilled lean-oil absorption system to scrub most of the VOC out of the vent gas. The lean oil used as an absorption fluid must have a high boiling point (low vapor pressure) to prevent significant levels of lean-oil vapor from being added to the scrubbed vent gas. A side stream of α-MBA and acetophenone (AP) mixture might make an effective scrubbing fluid, since the vapor pressure of this process stream is relatively low. A further advantage of using this process fluid is that the rich oil from the scrubber could be returned to the process for recovery of absorbed vapors instead of requiring a separate rich-oil stripping column. The cost-benefit ratio for this approach is expected to be significantly higher than that for option (a), unless the value of the recovered hydrocarbons is high enough to offset the larger capital costs and operating expenses. Properly designed and operated lean-oil scrubbing systems normally recover at least 95% of the VOC from a vent stream of this type.

(c) Use a packed-bed adsorption system (such as activated carbon or molecular sieves) to adsorb and remove the VOC. Use a twin-bed adsorption system to permit periodic regeneration of the adsorption bed and recovery of the adsorbed VOC. Adsorption systems of this type normally remove and recover at least 95% of the VOC from a vent stream of this type. One problem with this type of system is that styrene monomer in the vent gas might collect and polymerize in the pores of the adsorbent. If this occurred, the adsorbent material would become inactive and would have to be replaced with fresh adsorbent material. It is expected that this VOC emission reduction approach would have a higher cost-benefit ratio than those for alternatives (b).

16. Styrene Finishing Column Vent

The stream from vent A_{16} (Fig. III-6) is almost as large as the vent stream described in V-C-15 and is similar in composition; therefore the same control options apply. The principal VOC in the stream is styrene monomer. The most sensible approach would be to combine both vent streams in one common vent header and use a single emission control device (of larger scale) to control both vent emissions.

17. Hydrogenation Reactor Operating Vent

The relief valve in this vent line (A_{17}, Fig. III-6) is closed during normal operation and no vent gas or VOC is normally discharged. Abnormal or emergency conditions of reactor overpressure may occasionally create a vent gas discharge, but would be very rare. No emission control device is suggested.

18. Hydrogenation Reactor Activation Vent

Periodic activation of the hydrogenation catalyst with a dilute stream of hydrogen in nitrogen takes place to reestablish high levels of catalyst activity. Since the hydrogenation reactor is thoroughly purged to remove residual hydrocarbons prior to catalyst activation, the vent stream (A_{18}, Fig. III-6) of hydrogen in the nitrogen released during this periodic reactivation procedure does not contain significant amounts of VOC; therefore no emission control device is suggested.

D. OTHER PROCESSES

Since no other processes are currently being used domestically to produce propylene oxide, no attempt has been made to estimate VOC emissions, sources, or possible VOC emission control techniques for any other process.

E. FUGITIVE, STORAGE, AND SECONDARY EMISSIONS

Emission controls for fugitive storage, and secondary emissions are discussed in separate reports[6—8] that cover these emissions for the entire synthetic organic chemicals manufacturing industry.

F. REFERENCES*

1. C. W. Stuewe, IT Enviroscience, Inc., Trip Report for Visit to Dow Chemical Co., Plaquemine, LA, Nov. 16 and 17, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

2. Letter dated Oct. 5, 1979, from S. W. Fretwell, Oxirane Corp., Houston, TX, to Carl A. Peterson, Jr., IT Enviroscience, Inc.

3. C. A. Peterson, IT Enviroscience, Inc., Trip Report for Visit to Oxirane Chemical Co. (Channelview), Channelview, TX, Oct. 18, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

4. Letter dated Mar. 26, 1980, from S. W. Fretwell, Oxriane Corp., to J. R. Farmer, EPA.

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

Tables VI-1, VI-2, and VI-3 show the environmental impacts of reducing VOC emissions from the model plants representing the three alternate domestic routes for the manufacture of propylene oxide. The VOC emissions in each model plant were reduced by the use of the applicable control systems as described in Section V.

From an energy standpoint, typical uncontrolled model plants will consume heat in the range of 4.1 MJ/kg of product (chlorohydrination) through 14.9 MJ/kg of product (ethylbenzene hydroperoxide) to a high value of 28.3 MJ/kg of product (isobutane hydroperoxide). Corresponding electrical energy consumpton for these three processes is estimated at 1.0 to 1.3 MJ/kg of product.[1—3]

Heat released to the environment as low-level thermal energy will contain all the heat and electrical energy inputs listed above, in addition to the chemical energy released as heat of reaction. Because of the large amount of energy consumed in the manufacture of chlorine and caustic, the overall energy consumption (and release to the environment) for propylene oxide manufacture by the chlorohydrin process is actually higher than that for either of the hydroperoxide processes, even though the listed values for direct process energy consumption do not reflect this.

B. CONTROL COST IMPACT

No attempt has been made to assign or estimate capital or operating costs for the various control techniques described in this abbreviated report. Qualitative value judgements as to the expected ranges of cost-benefit ratios for the various control techniques have been inserted in the discussions on control options presented in Section V.

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Table VI-1. Environmental Impact of Controlled Model Plant Producing Propylene Oxide by the Chlorohydrination Process (68 Gg/yr)

Emission Source	Stream Designation (Fig.III-2)	Control Device or Technique	VOC Emission Reduction		
			Percent	Ratio (g/kg)*	Rate (Mg/yr)
Vent gas scrubber vent	A_1	Upgrade purity of propylene feedstock	70	7.175	487.9
Saponification cloumn vent	A_2	Fume water scrubber	95	0.0408	2.77
PO stripping column vent	A_3	Fume water scrubber	95	0.0057	0.39
Lights stripping column vent	A_4	Fume water scrubber	95	0.0057	0.39
PO final distillation column vent	A_5	Fume water scrubber	95	0.0057	0.39
DCP distillation column vent	A_6	Fume oil scrubber	90	0.00009	0.006
DCIPE stripping column vent	A_7	None			
Fugitive				Not estimated	
Storage and handling				Not estimated	
Secondary				Not estimated	
				7.234	491.9

*g of emission per kg of propylene oxide produced.

Table VI-2. Environmental Impact of Controlled Model Plant Producing Propylene Oxide by the Isobutane Hydroperoxide Process (417 Gg/yr)

Emission Source	Stream Designation (Fig.III-4)	Control Device or Technique	VOC Emission Reduction Percent	Ratio (g/kg)*	Rate (Mg/yr)
Oxidation reactor scrubber vent	A_1	Plant flare	98	1.725	719.3
TBA stripping column vent	A_2	Vent condenser	60	0.0024	1.0
Catalyst mix tank vent	A_3	None			
PO stripping column vent	A_4	Fume water scrubber	95	0.0176	7.3
Crude TBA recovery column vent	A_5	Fume water scrubber	95	0.0147	6.1
TBA wash-decant system vent	A_6	Plant flare	98	0.0069	2.9
Wastewater stripping column vent	A_7	Vent condenser	80	0.760	316.9
Solvent scrubber vent	A_8	Plant flare	98	0.617	257.5
Solvent recovery column vent	A_9	Plant flare	98	0.0004	0.17
Water stripping column vent	A_{10}	Plant flare	98	0.0012	0.51
Propylene glycol column and dipropylene glycol combined vent	A_{11}	Fume water scrubber	95	0.0551	23.0
Wastewater stripping column vent	A_{12}	Vent condenser	80	1.064	443.7
Plant furnace flue gas vents	A_{13}	None			
Fugitive				Not estimated	
Storage and handling				Not estimated	
Secondary				Not estimated	
				4.254	1756

*g of emission per kg of propylene oxide produced.

Table VI-3. Environmental Impact of Controlled Model Plant Producing Propylene Oxide by the Ethylbenzene Hydroperoxide Process (181 Gg/yr)

Emission Source	Stream Designation (Fig.III-6)	Control Device or Technique	VOC Emission Reduction Percent	Ratio (g/kg)*	Rate (Mg/yr)
Oxidation reactor scrubber vent	A_1	Selective adsorption (activated carbon)	80	1.297	234.8
FF evaporator vent	A_2	Plant flare	98	0.0048	0.9
Catalyst mix tank vent	A_3	None	0	0	0
Separation column vent	A_4	Pipe to fuel gas manifold	99	0.1584	28.7
Lights stripping column vent	A_5	Pipe to fuel gas manifold	99	0.1584	28.7
Propylene recovery column vent	A_6	Pipe to fuel gas manifold	99	0.1584	28.7
Product wash-decant system vent	A_7	Fume water scrubber	95	0.0005	0.1
Mixed HC wash-decant system vent	A_8	Plant flare	98	0.0014	0.3
EB wash-decant system vent	A_9	Plant flare	98	0.0013	0.2
EB stripping column vent	A_{10}	Plant flare	98	0.0014	0.3
Light HC stripping column vent	A_{11}	Plant flare	98	0.0014	0.3
α-MBA/AP stripping column vent	A_{12}	Plant flare	98	0.0076	1.4
Catalyst mix tank vent	A_{13}	None	0	0	0
Dehydration reactor system vent	A_{14}	Plant flare	98	0.0008	0.1
Light impurities stripping column vent	A_{15}	Plant flare	98	1.2152	219.9
Styrene finishing column vent	A_{16}	Plant flare	98	0.8134	147.2
Hydrogenation reactor operating vent	A_{17}	None	0	0	0
Hydrogenation reactor activation vent	A_{18}	None	0	0	0
Fugitive				Not estimated	
Storage and handling				Not estimated	
Secondary				Not estimated	
				3.820	691.4

of emission per kg of propylene oxide produced.

C. REFERENCES*

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

VII. SUMMARY

Propylene oxide is manufactured domestically from purified (chemical-grade) propylene by three separate processes. Each process uses propylene as the common building block for attachment of oxygen to form propylene oxide but uses different raw materials to accomplish this oxygen addition and generates different by-products, co-products, and waste streams. These different by-products and coproducts each have their own market and use patterns, and their market and sale values are highly significant in the overall economics and growth patterns for these three processes.

Domestic production of propylene oxide was estimated to be 927 Gg in 1978, with the current estimated total capacity for propylene oxide now listed as 1344 Gg/yr, giving an industrial utilization of nameplate capacity at 69%.

The principal domestic use for propylene oxide is in the manufacture of polyether polyols used for the manufacture of urethane foams. Other uses for propylene oxide include the manufacture of propylene glycol, dipropylene glycol, and various glycol ethers.

A. PROCESS CHARACTERISTICS[2—4]

1. Chlorohydrination Process[5]

The chlorohydrination process is the oldest of the currently practiced domestic processes for the manufacture of propylene oxide. When the manufacture of ethylene oxide was converted from the old chlorohydrination process to the newer direct oxidation process, the old chlorohydrination equipment became available for conversion for use in the propylene oxide process. This availability of equipment has permitted the growth of the propylene oxide chlorohydrination process with relatively small capital expenditures.

The chlorohydrination process generates relatively small quantities of by-products (principally dichloropropane and dichloroisopropyl/ether); so the successful operation of this process does not depend on a large market being found for co-products or by-products.

The chlorohydrination process consumes large quantities of chlorine and caustic (or lime). Slightly more than 1 mole of chlorine (Cl_2) and 2 moles of caustic (NaOH) are consumed in the manufacture of 1 mole of propylene oxide, generating slightly more than 2 moles of salt (NaCl) brine as a waste stream. Because of this large consumption of chlorine and caustic, the overall chlorohydrination process is an extremely extensive energy consumer, and the present high, and rapidly rising, costs of energy are making the economics of this process less attractive. Some smaller producers of propylene oxide using this process have already shut down their plants, and other small producers may do the same in the near future.

2. Isobutane Hydroperoxide Process[6]

The isobutane hydroperoxide process for the manufacture of propylene oxide is a relatively new production route in which isobutane is oxidized to the hydroperoxide by purified oxygen. The hydroperoxide, in turn, is used to epoxidize propylene to propylene oxide while forming the coproduct t-butyl alcohol (TBA).

Some t-butyl hydroperoxide is separated and purified as a coproduct for use elsewhere as an effective oxidizer in the production of other valuable oxygen-containing organic compounds. Approximately 2 moles of TBA are produced as a co-product for each mole of propylene oxide manufactured by this process. Some of this TBA is easily converted to isobutylene by passing the alcohol over a dehydration catalyst.[7]

Isobutane is readily available as a sidestream from an integrated refinery, and the price for purified isobutane is relatively low. Oxygen is readily separated from the air in standard designed air separation plants. Chemical-grade propylene is readily available from many integrated petrochemical-refinery complexes at standardized contract prices.

The co-products generated by the isobutane hydroperoxide process have a rapidly expanding market that can absorb all the co-products without strain; so manufacture of propylene oxide by this process is not limited by sales of the co-products. At present a major and expanding use for TBA is for blending into gasoline as an octane improver. Some TBA is used for chemical manufacture, such as t-butyl chloride and t-butyl phenol, etc. Some of the alcohol is being dehydrated to isobutylene, which can be reacted to form various alkylates useful in gasoline or can be purified and used in the manufacture of butyl rubber and polyisobutylene. A relatively new use for isobutylene is its reaction with methanol to form methyl t-butyl ether, a relatively new gasoline octane improver recently approved for use in unleaded gasoline.[7,8]

3. Ethylbenzene Hydroperoxide Process[9]

The ethylbenzene hydroperoxide process for the manufacture of propylene oxide is the latest commercial production route in which ethylbenzene is oxidized to the hydroperoxide by oxygen from the air. This hydroperoxide is then used to epoxidize propylene to propylene oxide while forming the coproduct α-methyl benzyl alcohol (α-MBA).

The α-MBA co-product does not have a large sales market, but it is dehydrated to styrene monomer by contacting the alcohol with a dehydration catalyst. The styrene monomer is then purified and sold to the large, well-established styrene monomer market for conversion into thermoplastic resins, synthetic rubber, latex emulsions, etc. A minor amount of acetophenone is produced as a by-product during the hydroperoxide production step, and this material is separated and reacted with hydrogen over a hydrogenation catalyst to convert the acetophenone to additional α-MBA.

It would, perhaps, be more accurate to describe the ethylbenzene hydroperoxide process as a process for the manufacture of styrene monomer with propylene oxide as a co-product, since this process yields about 2.5 kg of styrene monomer for each kg of propylene oxide produced. The major constraints on the production of propylene oxide and styrene monomer by this process at the present time are the availability and price of aromatic hydrocarbons (principally benzene and toluene) from which ethylbenzene is produced. Petroleum feedstocks, particularly those streams rich in aromatics, are in great demand for use in raising the octane ratings of unleaded gasoline. Styrene monomer is a relatively mature, large-volume, commodity hydrocarbon, and its growth rate has been estimated at 4 to 6% in the 1976—1980 period, with production operating at about 78% of total plant capacity due to aromatics supply shortages.[10]

B. PROCESS EMISSION CHARACTERISTICS

1. Chlorohydrination Process[5]

The chlorohydrin process has one large vent stream that contains 99% of the process VOC emissions generated in the uncontrolled model plant (see Table IV-1). The principal source of the VOC being released by this vent stream is the propane contained in the chemical-grade propylene fed to the chlorohydrination reactor. Dow has studied this emission source, and they state that the most cost-effective technique for reducing the emission is to use high-purity (polymer-grade) propylene as reactor feed, thereby eliminating most of the propane that is released as VOC. Other techniques that could be used to reduce emissions from this vent include thermal oxidation (fume incinerator or flare) or the use of a lean-oil scrubbing system to absorb and recover the hydrocarbons from this vent gas. Controlled versus uncontrolled emissions for this process are summarized in Table VII-1.

2. Isobutane Hydroperoxide Process[6]

The isobutane hydroperoxide process has three fairly large vent streams that, in total, contain over 96% of the process VOC emissions generated in the uncontrolled model plant (see Table IV-2). The first stream is emitted from the scrubber system on the oxidation reactor, with the principal VOC being a mixture of isobutane and TBA. The VOC is relatively dilute, with inert gases making up over 75 wt % of the total stream. These inert gases (principally argon) enter the oxidation reactor with the oxygen from the air separation plant and sweep the organic vapors out of the oxidation reactor. Techniques that could be used to reduce the VOC emissions from this vent include converting the TBA scrubber to a lean-oil scrubber with associated recovery column, installing an activated-carbon recovery system to adsorb and recover the VOC, or sending the vent gas to a thermal oxidation system (fume incinerator or flare) to oxidize the VOC.

The second stream is emitted from the vent on the wastewater stripping column used to strip isobutylene and TBA out of the wastewater generated by washing of the product stream after dehydration of TBA to isobutylene. The VOC in this vent consists principally of isobutylene, along with some lesser amounts of TBA and acetone. Techniques that could be used to reduce the VOC emissions include the use of a refrigerated vent condenser to recover most of the contained VOC or the delivery of the vent gas to a thermal oxidation system (fume incinerator or flare) to oxidize the VOC.

Table VII-1. Emission Summary for Model Plant Producing Propylene Oxide by the Chlorohydrination Process (68 Gg/yr)[a]

			VOC Emissions			
			Uncontrolled		Controlled	
Emission Source	Stream Designation (Fig.III-2)	Control Device or Technique	Ratio (g/kg)[b]	Rate (kg/hr)	Ratio (g/kg)[b]	Rate (kg/hr)
Vent gas scrubber vent	A_1	Upgrade purity of propylene feedstock	10.25	79.57	3.07	23.87
Saponification column vent	A_2	Fume water scrubber	0.043	0.33	0.0021	0.017
PO stripping column vent	A_3	Fume water scrubber	0.006	0.05	0.0003	0.0025
Lights stripping column vent	A_4	Fume water scrubber	0.006	0.05	0.0003	0.0025
PO final distillation column vent	A_5	Fume water scrubber	0.006	0.05	0.0003	0.0025
DCP distillation column vent	A_6	Fume oil scrubber	0.0001	0.0008	0.00001	0.0000
DCIPE stripping column vent	A_7	None	0.000004	0.00003	0.000004	0.0000
Fugitive			Not estimated			
Storage and handling			Not esitmated			
Secondary			Not estimated			
			10.31	80.05	3.087	23.90

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[a] See ref 5.

[b] g of emission per kg of propylene oxide produced.

The third stream is emitted from the vent on the wastewater stripping column used to strip crude acetone out of the combined wastewater streams from the TBA purification system and the dilute caustic scrubber on the vent of the oxidation reactor. The VOC in the vent stream consists principally of acetone, along with some isobutane and methanol. These VOC emissions may be controlled by using a refrigerated vent condenser to recover most of the contained VOC. An alternative technique that could be used is the delivery of the vent gas to a thermal oxidizer system (fume incinerator or flare) for oxidation of the VOC. Controlled versus uncontrolled emissions for this process are summarized in Table VII-2.

3. Ethylbenzene Hydroperoxide Process[9]

The ethylbenzene hydroperoxide process has three moderately large vent streams that, in total, contain over 84% of the process VOC emissions generated in the uncontrolled model plant (see Table IV-3). The first stream comes from the vent on the scrubber system used to recovery VOC from the oxidation reactor vent gas. The VOC in this scrubber vent gas is extremely dilute, but the amount of gas being vented is extremely large; therefore the total amount of VOC in the stream is fairly large. Because this VOC is extremely dilute, the only possible technique for its reduction is to use an adsorption technique (activated carbon or molecular sieves) to remove and recover this VOC. Adsorption techniques for treating extremely dilute VOC in vent gas streams are quite expensive because of high capital costs and large operating costs. It is believed that cost-benefit ratios would be very high for any attempt to reduce the VOC emissions from this scrubber system. An alternative approach that might be attempted is the use of oxygen from an air separation plant in place of air in the oxidation reactor, thereby radically reducing the amount of inert gas being vented and reducing the contained VOC. This technique would be extremely difficult and expensive to retrofit on an existing facility; but, if a new plant for the ethylbenzene hydroperoxide process were constructed, this process change might be a relatively cost-effective technique for reduction of VOC emissions from this source.

The second and third large VOC emission sources are the vent gas exhausts on the light impurities stripping column and the styrene finishing column. Both these columns are located in the styrene finishing area and close to each other, as well as being tied together operation-wise. The vent gases are relatively dilute, but contain chemically similar VOC emissions (ethylbenzene and styrene monomer).

Table VII-2. Emission Summary for the Model Plant Producing Propylene Oxide by the Isobutane Hydroperoxide Process (417 Gg/yr)[a]

Emission Source	Stream Designation (Fig.III-4)	Control Device or Technique	VOC Emissions			
			Uncontrolled		Controlled	
			Ratio (g/kg)[b]	Rate (kg/hr)	Ratio (g/kg)[b]	Rate (kg/hr)
Oxidation reactor scrubber vent	A_1	Plant flare	1.76	83.8	0.0352	1.676
TBA stripping column vent	A_2	Vent condenser	0.004	0.19	0.0014	0.114
Catalyst mix tank vent	A_3	None	0.000012	0.0006	0.000012	0.0006
PO stripping column vent	A_4	Fume water scrubber	0.0185	0.88	0.00093	0.044
Crude TBA recovery column vent	A_5	Fume water scrubber	0.0155	0.74	0.00078	0.037
TBA wash-decant system vent	A_6	Plant flare	0.00174	0.34	0.00036	0.017
Wastewater stripping column vent	A_7	Vent condenser	0.95	45.2	0.190	9.04
Solvent scrubber vent	A_8	Plant flare	0.63	30.0	0.013	0.60
Solvent recovery column vent	A_9	Plant flare	0.00046	0.02	0.00001	0.0004
Water stripping column vent	A_{10}	Plant flare	0.0013	0.06	0.00002	0.0012
Propylene glycol column and dipropylene glycol column combined vent	A_{11}	Fume water scrubber	0.058	2.76	0.0029	0.138
Wastewater stripping column vent	A_{12}	Vent condenser	1.33	63.3	0.266	12.66
Plant furnace flue gas vents	A_{13}	None	0.040	1.90	0.040	1.90
Fugitive				Not estimated		
Storage and handling				Not estimated		
Secondary				Not estimated		
			4.81	229.17	0.551	26.25

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[a] See ref 6.

[b] g of emission per kg of propylene oxide produced.

The most simple and most practical technique for reducing these VOC emissions would be to tie the column vents together in one common vent header and direct its output to a thermal oxidation system (fume incinerator or flare) for destruction of the contained VOC. A possible alternative technique might be the installation of a refrigerated vent condenser on the vent header outlet to recover contained VOC. Because of the dilution of the VOC in this vent stream, it is believed that the use of a vent condenser would not remove as much VOC or be as cost effective as a thermal oxidation system.

Controlled versus uncontrolled emissions for this process are summarized in Table VII-3.

C. DATA BASE

The process emissions for the propylene oxide model plants are based on information furnished by Dow Chemical Co.[5] and by Oxirane Chemical Co.[6,9] Also, the process flowsheets were developed from published reports on propylene oxide by Stanford Research Institute,[1—4] along with an understanding of the process chemistry and physical property data on the raw materials, intermediates, products, coproducts, and by-products. No attempts were made to estimate emissions due to fugitive, storage and handling, or secondary sources for this abbreviated report.

D. INDUSTRIAL EMISSIONS ESTIMATE

Based on the estimated propylene oxide production of 985 Gg for 1979 and based on the current capacity ratio of 746 Gg/yr by chlorohydrination, 417 Gg/yr by isobutane hydroperoxide, and 181 Gg/yr by ethylbenzene hydroperoxide, as well as on information on current industry emission control practices, the total emission of VOC during the manufacture of propylene oxide in 1979 was estimated to be about 5.8 Gg. It is believed that over 95% of the total emissions were generated by the chlorohydrination process, with the two hydroperoxide processes together generating less than 5% of the total VOC emitted.

Table VII-3. Emission Summary for Model Plant for Production of Propylene Oxide by the Ethylbenzene Hydroperoxide Process (181 Gg/yr)[a]

			VOC Emissions			
			Uncontrolled		Controlled	
Emission Source	Stream Designation (Fig.III-6)	Control Device or Technique	Ratio (g/kg)[b]	Rate (kg/hr)	Ratio (g/kg)[b]	Rate (kg/hr)
Oxidation reactor scrubber vent	A_1	Selective adsorption (activated carbon)	1.61	33.5	0.32	6.7
FF evaporator vent	A_2	Plant flare	0.0051	0.11	0.000255	0.0055
Catalyst mix tank vent	A_3	None	Trace	Trace	Trace	Trace
Separation column vent	A_4	Pipe to fuel gas manifold	0.16	3.31	0.0016	0.0331
Lights stripping column vent	A_5	Pipe to fuel gas manifold	0.16	3.31	0.0016	0.0331
Propylene recovery column vent	A_6	Pipe to fuel gas manifold	0.16	3.31	0.0016	0.0331
Product wash-decant system vent	A_7	Fume water scrubber	0.0005	0.01	0.000025	0.0005
Mixed HC wash-decant system vent	A_8	Plant flare	0.0015	0.03	0.00003	0.0006
EB wash-decant system vent	A_9	Plant flare	0.0014	0.03	0.00003	0.0006
EB stripping column vent	A_{10}	Plant flare	0.0015	0.03	0.00003	0.0006
Light HC stripping column vent	A_{11}	Plant flare	0.0015	0.03	0.00003	0.0006
α MBA-AP stripping column vent	A_{12}	Plant flare	0.0080	0.17	0.00040	0.0085
Catalyst mix tank vent	A_{13}	None	Trace	Trace	Trace	Trace
Dehydration reactor system vent	A_{14}	Plant flare	0.0008	0.02	0.00002	0.0004
Light impurities stripping column vent	A_{15}	Plant flare	1.24	25.7	0.0248	0.514
Styrene finishing column vent	A_{16}	Plant flare	0.83	17.2	0.0166	0.344

Table VII-3. (Continued)

			VOC Emissions			
			Uncontrolled		Controlled	
Emission Source	Stream Designation (Fig.III-6)	Control Device or Technique	Ratio (g/kg)[b]	Rate (kg/hr)	Ratio (g/kg)[b]	Rate (kg/hr)
Hydrogenation reactor operating vent	A_{17}	None	Normally 0	Normally 0	0	0
Hydrogenation reactor activation vent	A_{18}	None	Normally C	Normally 0	0	0
Fugitive				Not estimated		
Storage and handling				Not estimated		
Secondary				Not estimated		
9			4.12	86.6	0.367	7.67

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[a] See ref 9.

[b] g of emission per kg of propylene oxide produced.

E. REFERENCES*

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

APPENDIX A

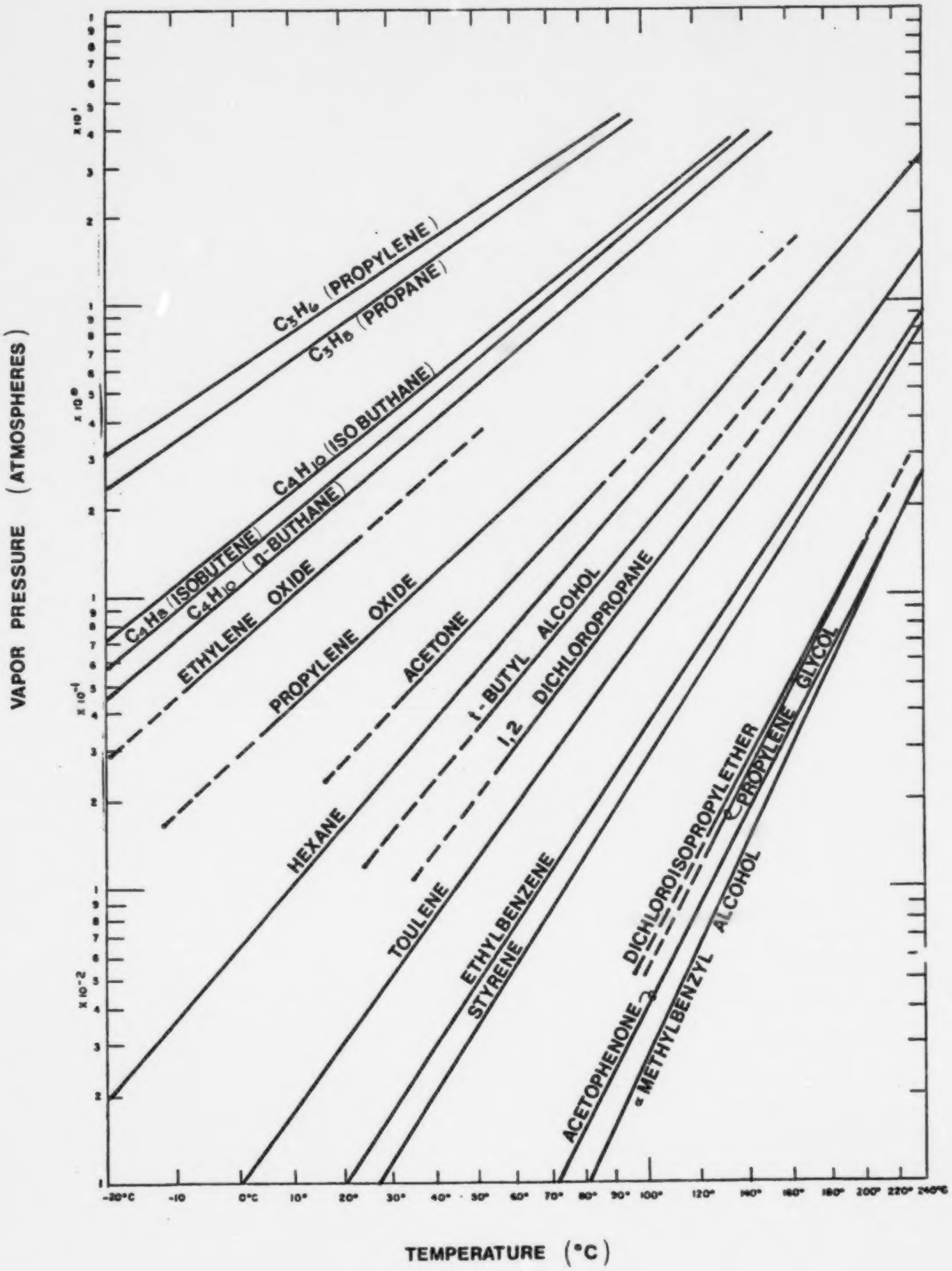

Fig. A-1. Vapor Pressure vs. Temperature

Appendix B

EXISTING PLANT CONSIDERATIONS

A. EXISTING PLANT CHARACTERIZATION

Information has been received regarding control devices or techniques from the following three manufacturers of propylene oxide:

1. Chlorohydrination Process[1]

The Dow Chemical Co., Plaquemine, LA, has a nominal plant capacity of 154 Gg/yr of propylene oxide. The information available on this plant is summarized in Table B-1. This plant information is based on its 1977 configuration and capacity.

2. Isobutane Hydroperoxide Process[2]

Oxirane Corporation, Bayport, TX, has a nominal plant capacity of 417 Gg/yr of propylene oxide. The information available on this plant is summarized in Table B-2. This plant contains 10 different units built over a number of different years. The data presented represent the current technology of the newest unit. In terms of air emissions the model plant contains several vent streams that are not present in the Oxirane process.[3]

3. Ethylbenzene Hydroperoxide Process[4]

Oxirane Chemical Co., Channelview, TX, has a nominal plant capacity of 181 Gg/yr of propylene oxide. The information available on this plant is summarized in Table B-3. This plant was started up in 1977.

B. RETROFITTING CONTROLS

The control devices and techniques discussed in Sect. V may not be applicable to existing plants. Retrofitting control devices or techniques into existing plants brings up such questions as: Is there space in the existing plant to fit in and install the new hardware required? Do the operating characteristics of the emission control device fit the operating characteristics of the process equipment? Are the operating characteristics and design limitations of the control device compatible with the upset or emergency conditions that the process might encounter? Are the startup and shutdown characteristics of the control device compatible with the startup and shutdown requirements of the process? Are extensive process modifications needed to accomplish significant emission reductions? Where changes in feedstock or intermediates are needed to reduce

Table B-1. Existing Plant for the Manufacture of Propylene Oxide by the Chlorohydrination Process (154 Gg/yr) (Dow Chemical Co., Plaquemine, LA)[a]

Emission Source	Stream Designation (Fig. III-2)	Control Device or Technique	VOC Emissions Ratio (g/kg)[b]	VOC Emissions Rate (kg/hr)
Vent gas scrubber vent	A_1 } Combined in report	Vent scrubber used to remove HCl and Cl_2; no device used	10.27	180.5
Saponification column vent	A_2			
PO stripping column vent	A_3 } Combined in report	Vent scrubbers (packed columns), with water used as scrubbing fluid (all vents directed to a common vent header before control device)	0.00031	0.054
Lights stripping column vent	A_4			
PO final distillation column vent	A_5			
DCP distillation column vent	A_6			
DCIPE stripping column vent	A_7			
Fugitive		Estimated fugitive losses	0.0029	0.052
Storage and handling		Vent scrubbers (packed column) with water used as scrubber fluid	0.0059	0.104
Secondary	Organic liquid wastes	Thermal oxidizer with alkaline water vent scrubber	0.0059	0.104
			10.29	180.8

---

[a] See ref 1.

[b] g of emission per kg of propylene oxide produced.

Table B-2. Existing Plant for the Manufacture of Propylene Oxide by the Isobutane Hydroperoxide Process (417 Gg/yr)(Oxirane Corp., Bayport, TX)[a]

Emission Source	Stream Designation (Fig.III-4)	Control Device or Technique	VOC Emissions	
			Ratio (g/kg)[b]	Rate (kg/hr)
Oxidation reactor scrubber vent	A_1	Fumes from scrubber sent to flare	Quantities not listed	
TBA stripping column vent	A_2	None (pressure control)	0.012	5.69
Catalyst mix tank vent	A_3	None	Trace	Trace
PO stripping column vent	A_4	Plant flare	Quantities not listed	
Crude TBA recovery column vent	A_5	Plant flare	Quantities not listed	
TBA wash-decant system vent	A_6	Plant flare	Quantities not listed	
Wastewater stripping column vent	A_7	Plant flare	Quantities not listed	
Solvent scrubber vent	A_8 } Combined in report	None	0.0215	1.023
Solvent recovery column vent	A_9			
Water stripping column vent	A_{10} } Combined in report	None	0.0579	2.76
Propylene glycol column and dipropylene glycol column combined vent	A_{11}			
Wastewater stripping column vent	A_{12}	Plant flare	Quantities not listed	
Plant furnace flue gas vent	A_{13}	None	Quantities not listed	
Fugitive			No information provided	
Storage and handling			Some data presented, but quantities not summarized	
Secondary			Secondary streams listed, but emissions not determined	

---

[a] See ref 2.

[b] g of emission per kg of propylene oxide produced.

Table B-3. Existing Plant for the Manufacture of Propylene Oxide by the Ethylbenzene Hydroperoxide Process (181 Gg/yr) (Oxirane Chemical Co., Channelview, TX)[a]

Emission Source	Stream Designation (Fig.III-6)	Control Device or Technique	VOC Emissions	
			Ratio (g/kg)[b]	Rate (kg/hr)
Oxidation reactor scrubber vent	A_1 Combined in report	Oil scrubber and water scrubber used to control emissions and recover product	0.724	15.0
FF evaporator vent	A_2			
Catalyst mix tank vent	A_3	Plant flare	Flare emissions not stated	
Separation column vent	A_4	Plant fuel gas manifold	No emissions stated	
Lights stripping column vent	A_5	Plant fuel gas manifold	No emissions stated	
Propylene recovery column vent	A_6	Plant fuel gas manifold	No emissions stated	
Product wash-decant system vent	A_7	Backpressure control valve and nitrogen pad	Trace	Trace
Mixed HC wash-decant system vent	A_8	Backpressure control valve and nitrogen pad	Trace	Trace
EB wash-decant system vent	A_9	Backpressure control valve and nitrogen pad	Trace	Trace
EB stripping column vent	A_{10} Combined in report	Plant flare	Flare emissions not stated	
Light HC stripping column vent	A_{11}			
α MBA-AP stripping column vent	A_{12}			
Catalyst mix tank vent	A_{13}	None stated	None stated	
Dehydration reactor system vent	A_{14} Combined in report	Plant flare	Flare emissions not stated	
Light impurities stripping column vent	A_{15}			
Styrene finishing column vent	A_{16}			

Table B-3. (Continued)

Emission Source	Stream Designation (Fig. III-6)	Control Device or Technique	VOC Emissions	
			Ratio (g/kg)[b]	Rate (kg/hr)
Hydrogenation reactor operating vent	A_{17}	Plant fuel gas manifold	No emissions stated	
Hydrogenation reactor activation vent	A_{18}	Plant flare	Flare emissions not stated	
Fugitive			No information provided	
Storage and handling			No information provided	
Secondary		Secondary waste streams described	No air emission data provided	

---

[a] See ref 3.

[b] g of emission per kg of propylene oxide produced.

process emissions, are the changed feedstock or intermediates readily available at reasonable prices? Specific comments on retrofitting controls to existing processes are as follows:

1. Chlorohydrination Process

The one major retrofit operation most likely to fit this process is the conversion from use of lower purity (chemical grade) propylene to the use of higher purity (polymer grade) propylene. Both grades of propylene are available from major propylene suppliers. The high-purity (polymer-grade) propylene commands a premium price (usually about 1¢/lb) over the lower purity (chemical-grade) feedstock, but its use would reduce total plant emissions by at least 70%. Specific supply situations at individual manufacturing plants would have to be reviewed to see whether this approach is feasible for each producer using the chlorohydrination process.

An alternative approach would be the installation of a thermal oxidizer with an alkaline vent gas scrubbing system to destroy the propane being vented from the chlorohydrination reactor. This equipment installation would have to be reviewed to see whether it could be fitted into the existing plant.

2. Isobutane Hydroperoxide Process

Retrofitting control devices to existing plants using this process is likely to be difficult. The first major emission source is the vent stream from the scrubbers on the oxidation reactor. The simplest technique for control of this emission, as currently practiced, is to pipe the vent gas to a thermal oxidizer system (plant flare), with the oxidizer system assumed to have sufficient spare capacity to handle this stream. Other techniques, such as conversion of the TBA scrubber to a lean-oil absorption-recovery system, are likely to involve space (location) problems, as well as being much more expensive.

The second large vent stream is emitted from the vent on the wastewater stripping column in the isobutylene conversion process. The simplest retrofit approach for this vent, as currently practiced, is to collect the vent gas in a header and feed it to a thermal oxidizer system (plant flare). Again to be successful, the oxidizer system must have enough spare capacity to handle this vent gas stream.

The third large vent stream comes from the vent on the combined wastewater stripper. Again, the simplest retrofit approach for this stream, as currently practiced, is the installation of vent gas piping to the header of the plant thermal oxidizer (plant flare).

3. Ethylbenzene Hydroperoxide Process

Emissions from the ethylbenzene hydroperoxide process are now being fairly well controlled. The first major vent stream comes from the scrubbers on the oxidation reactors, and the VOC in this vent gas is extremely dilute. Attempts to retrofit an effective adsorption system on this vent gas stream are likely to be very difficult and expensive. Any attempt to further improve the performance of the existing vent gas scrubbers is also likely to be very difficult and expensive.

The second and third large VOC emission streams come from the vent on the vacuum distillation columns in the styrene purification section. The current emission control technique for these sources is to pipe the vent streams through a common header to the plant thermal oxidation system (plant flare).

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

REPORT 2

ACRYLONITRILE

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Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

November 1980

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch² (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Acrylonitrile was selected for in-depth study because preliminary estimates indicated that its manufacturing process causes higher estimated emissions of volatile organic compounds (VOC) than any other process in the synthetic organic chemicals manufacturing industry. The growth rate for the production of acrylonitrile is expected to be higher than the industry average. Acrylonitrile is highly toxic and has been declared[1] to be a potential carcinogen.

Acrylonitrile is a liquid under ambient conditions but is sufficiently volatile for gaseous emissions to occur during production (see Appendix A for pertinent properties). The emissions from acrylonitrile production consist of propane, propylene, acetonitrile, acrylonitrile, and hydrogen cyanide. Propane and propylene account for about 86% of the total emissions.

B. USAGE AND GROWTH

Table II-1 shows acrylonitrile end uses and the expected growth rates. The predominant use for acrylonitrile is in the production of acrylic fibers, mainly for the apparel industry. Other major end uses of acrylic fiber include carpeting and home furnishings, e.g., blankets, draperies, and upholstery.[2]

The domestic acrylonitrile production capacity was 980,000 Mg/yr at the end of 1977. Production was 754,600 Mg in 1977,[3] or about 77% of capacity. Operating capacity was reduced to 900,000 Mg/yr early in 1978, when one producer shut down a unit[4] and another reportedly increased capacity a small amount.[5] Demand will exceed current capacity by 1981 if an anticipated growth rate of 8% is realized.[3]

C. DOMESTIC PRODUCERS

Four producers were operating six acrylonitrile plants in 1977. Table II-2 lists the producers with their 1977 capacities, and Fig. II-1 shows the plant locations.

Ammoxidation of propylene accounts for all current domestic production of acrylonitrile, although catalytic reaction of acetylene and hydrogen cyanide was used as a production method until late 1970. Other processes that have been used commercially include catalytic dehydration of ethylene cyanohydrin and catalytic

Table II-1. Acrylonitrile Usage and Growth[a]

End Use	Percent of Production (1977)	Average Annual Growth (1977-1980) (%)
Acrylic fibers	67.2	7
Acrylonitrile-butadiene-styrene copolymer (ABS) and styrene-acrylonitrile polymer (SAN) resins	19.7	8
Nitrile elastomers	5.6	4
Miscellaneous[b]	7.5	24

[a] See ref 3.

[b] Includes adiponitrile, acrylamide, nitrile barrier resins, and other products.

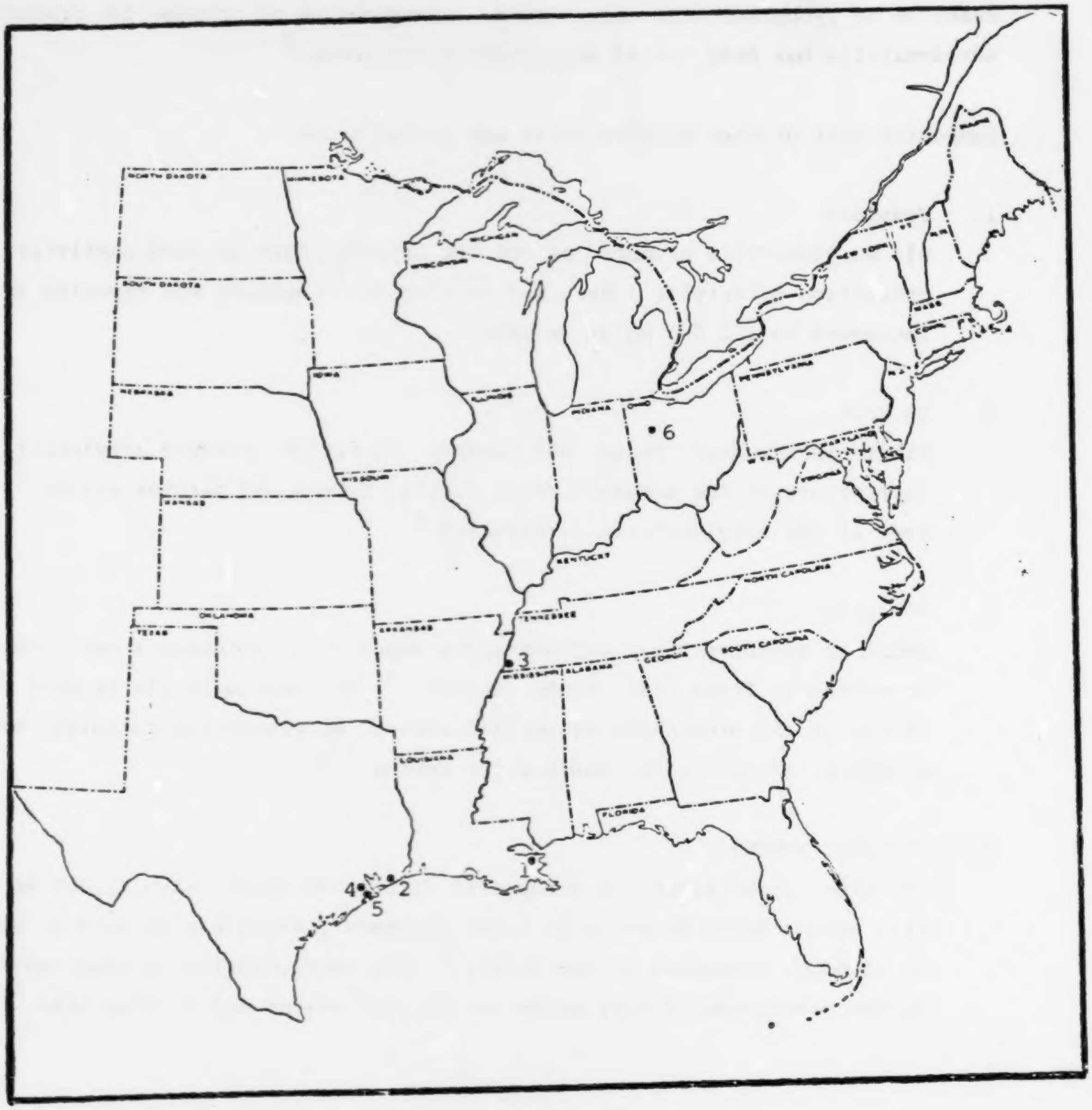
Table II-2. Acrylonitrile Capacity[a]

Plant	1977 Capacity ($\times 10^3$ Mg/yr)
Cyanamid, New Orleans, LA	109[b]
Du Pont, Beaumont, TX	159
Du Pont, Memphis, TN	136
Monsanto, Alvin, TX	204
Monsanto, Texas City, TX	191[c]
Vistron, Lima, OH	181
Total	980

[a] See ref 6.

[b] Cyanamid's capacity was reportedly increased to 120 $\times 10^3$ Mg/yr in 1978 (ref 5).

[c] Monsanto brought their Texas City plant on-stream in 1977.



1. American Cyanamid, New Orleans, Louisiana
2. Dupont Co., Beaumont, Texas
3. Dupont Co., Memphis, Tennessee
4. Monsanto Co., Alvin, Texas
5. Monsanto Co., Texas City, Texas
6. Vistron, Lima, Ohio

Fig. II-1. Acrylonitrile Manufacturing Locations

reaction of propylene with nitric acid. Ammoxidation of propane for producing acrylonitrile has been tested on a pilot-plant scale.[2]

Companies that produce acrylonitrile are listed below:

1. Cyanamid
   All acrylonitrile produced at the New Orleans plant is used captively in the production of acrylic fibers and acrylamide.[2] Capacity was reported to have increased to 120,000 Mg/yr in 1978.[5]

2. Du Pont
   Plants in Beaumont, Texas, and Memphis, Tennessee, produce acrylonitrile for captive use in the manufacture of acrylic fibers and barrier resins.[2,3] Some of the acrylonitrile is marketed.[2]

3. Monsanto
   Monsanto expanded their acrylonitrile capacity by bringing a new plant on-stream at Texas City, Texas, in 1977.[6] The acrylonitrile is used captively in the production of acrylic fibers, acrylonitrile butadiene styrene plastics, adiponitrile, and barrier resins.[2,3]

4. Vistron (SOHIO)
   The Lima, Ohio, plant has a capacity of 181,000 Mg/yr, with 45,000 Mg of that amount being produced by older equipment, which can be used or placed on standby, depending on the market.[6] The acrylonitrile is used captively in the production of acrylamide and barrier resins and is also sold.[2,3]

D. REFERENCES*

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2. J. L. Blackford, "Acrylonitrile," pp. 607.5031B--607.5032S in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (June 1974).
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III. PROCESS DESCRIPTION

A. INTRODUCTION

All domestic acrylonitrile is produced by the ammoxidation of propylene by the SOHIO process, which is predominant worldwide although other processes are used by some foreign producers.[1] Over 95% of the world's installed capacity for acrylonitrile production uses the ammoxidation of propylene; and all new capacity, either planned or under construction, will use ammoxidation of propylene.[2]

B. SOHIO PROCESS

1. Basic Process

Acrylonitrile is produced by the following chemical reaction:

$$\underset{\text{(Propylene)}}{\mathrm{CH_2{=}CH{-}CH_3}} + \underset{\text{(Ammonia)}}{\mathrm{NH_3}} + \underset{\text{(Oxygen)}}{3/2\ \mathrm{O_2}} \longrightarrow \underset{\text{(Acrylonitrile)}}{\mathrm{CH_2{=}CH{-}CN}} + \underset{\text{(Water)}}{\mathrm{3H_2O}}$$

The process flow diagram shown in Fig. III-1 represents a typical process.[3]

Air, ammonia, and propylene (Streams 1, 2, and 3) are fed to a gas fluid-bed catalytic reactor that operates at 135 to 310 kPa and 400 to 510°C. The reactor temperature is controlled by internal cooling coils, which generate about 75% of the process steam required by the plant. The remainder is generated in a waste heat boiler, where the gases from the reactor (Stream 4) are cooled from 510 to 230°C. The cooled reactor gases (Stream 5) are further cooled in the quench neutralizer, and the ammonia and catalyst fines are removed. The quenched and neutralized reactor gases (Stream 6) go to the absorber, where acrylonitrile, acetonitrile, and hydrogen cyanide (HCN) are recovered by absorption in water; the absorber vent gas (Vent A) is vented to the atmosphere or to a control device.[4,5]

The absorber bottoms (Stream 7) go to a recovery column, where crude acrylonitrile (Stream 8) is separated from crude acetonitrile (Stream 9) and sent to the crude acrylonitrile storage. The crude acetonitrile (Stream 9) goes to the acetonitrile column for separation of the water (Stream 10), which is then recycled to the absorber; the dried acetonitrile (Stream 11) goes overhead and is sent to the acetonitrile purification column for final purification.[4--6]

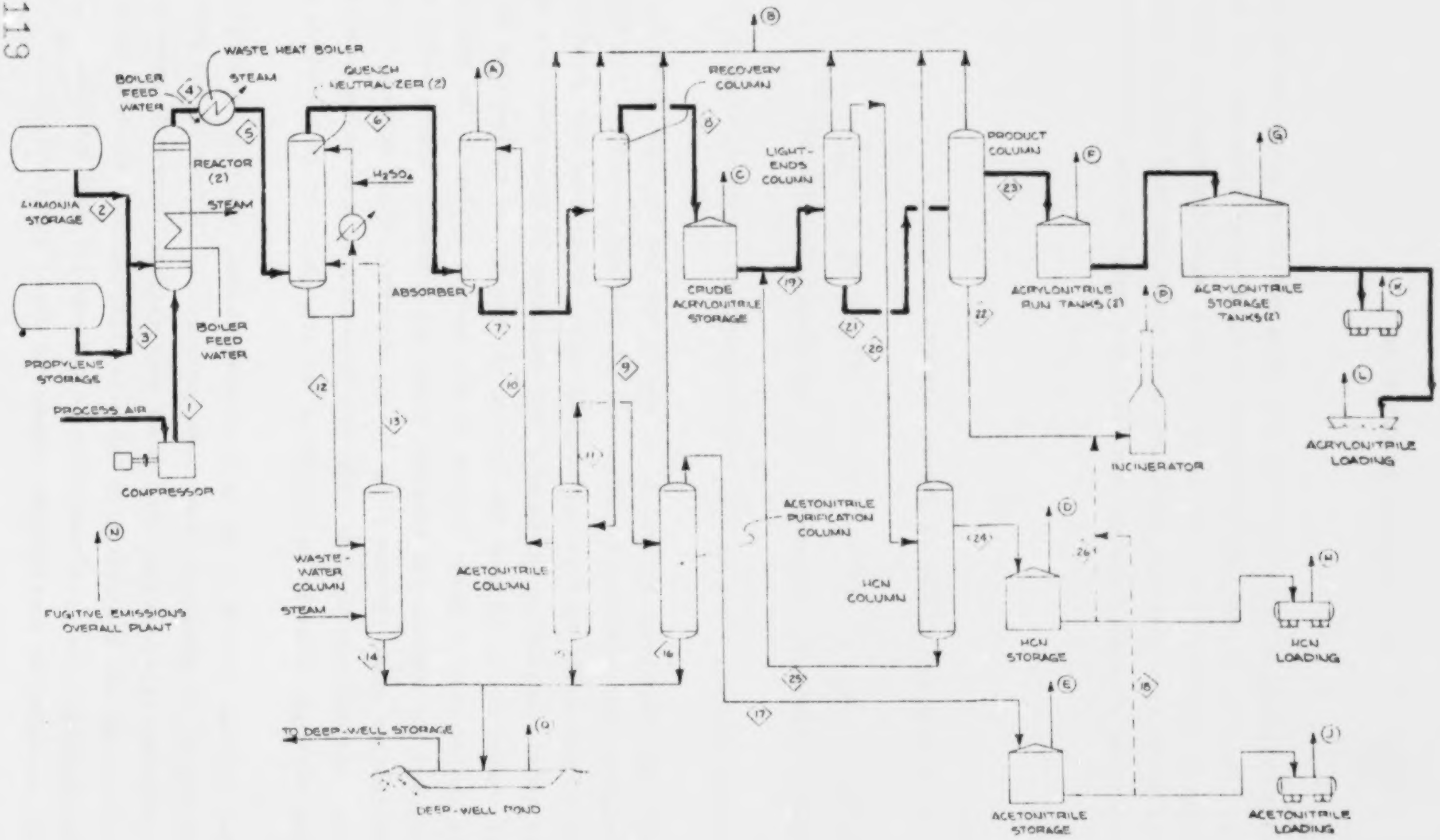
WASTE HEAT BOILER
BOILER FEED WATER
STEAM
4
5
REACTOR (2)
STEAM
AMMONIA STORAGE
2
PROPYLENE STORAGE
3
BOILER FEED WATER
PROCESS AIR
1
COMPRESSOR
QUENCH NEUTRALIZER (2)
6
H_2SO_4
A
ABSORBER
7
12
13
10
9
11
RECOVERY COLUMN
8
B
C
CRUDE ACRYLONITRILE STORAGE
19
LIGHT-ENDS COLUMN
21
20
PRODUCT COLUMN
23
22
F
ACRYLONITRILE RUN TANKS (2)
P
INCINERATOR
G
ACRYLONITRILE STORAGE TANKS (2)
K
L
ACRYLONITRILE LOADING
N
FUGITIVE EMISSIONS OVERALL PLANT
WASTE-WATER COLUMN
STEAM
14
ACETONITRILE COLUMN
15
16
ACETONITRILE PURIFICATION COLUMN
HCN COLUMN
24
D
26
HCN STORAGE
H
HCN LOADING
25
17
18
E
ACETONITRILE STORAGE
J
ACETONITRILE LOADING
TO DEEP-WELL STORAGE
Q
DEEP-WELL POND

Fig. III-1. Process Flow Diagram for Uncontrolled SOHIO Acrylonitrile Process for Model Plant

A portion of the quench water (Stream 12) from the quench neutralizer is sent to the wastewater column, where volatile organics (Stream 13) are separated by steam stripping and are recycled to the quench neutralizer. The bottoms from the wastewater column (Stream 14), which contain some of the catalyst, ammonium sulfate, and heavy organics, are sent to the deep-well pond along with the bottoms from the acetonitrile column (Stream 15) and from the acetonitrile purification column (Stream 16). The overhead from the acetonitrile purification column (Stream 17) goes to acetonitrile storage and can be sold if it meets specifications. If there is no demand for acetonitrile or if it is off-specifications, it is sent (Stream 18) to an incinerator.[4--6]

Crude acrylonitrile (Stream 19) is separated by the light-ends column into the light ends (Stream 20), which are sent to the HCN column; the acrylonitrile bottoms (Stream 21) go to the product column. There the heavy impurities (Stream 22) are removed from the product acrylonitrile (Stream 23). The heavy impurities (Stream 22) are disposed of in the incinerator.[4--6]

The light ends (Stream 20) sent to the HCN column are separated into hydrogen cyanide (HCN) (Stream 24), which can be sold if it meets sales specifications, and the bottoms (Stream 25), which are recycled as a portion of the feed to the light-ends column. The HCN that does not meet specifications or that cannot be sold because of lack of demand (Stream 26) goes to the incinerator for disposal.

The wastewater sent to the deep-well pond contains ammonium sulfate, catalyst fines, organic polymers, and other organics. After the solids settle out in the deep-well pond, the runoff is injected into deep wells.[3,4,6]

The absorber gas from Vent A is the largest emission and contains the following: unreacted oxygen and nitrogen from the air (Stream 1), which is fed as a reactant; any propane and unreacted propylene from the propylene feed (Stream 3); the carbon dioxide and carbon monoxide formed by side reactions; and acrylonitrile, acetonitrile, hydrogen cyanide, and other organics carried with the nitrogen from the absorber. Other emissions are the vent gases (Vents B) from the various columns: recovery, acetonitrile, acetonitrile purification, light-ends, product, and HCN.[3,4,6]

Storage emission sources (Vents C through G) include crude acrylonitrile, hydrogen cyanide, acetonitrile, and acrylonitrile storage. Handling emissions (Vents H through L) result from loading HCN, acetonitrile, and acrylonitrile into railroad tank cars and acrylonitrile into barges.

Fugitive emissions (N) occur when leaks develop in valves or in pump or compressor seals and when relief valves open to relieve a pressure buildup. When the process pressures are higher than the cooling-water pressure, acrylonitrile and other organics can leak into the cooling water and escape as fugitive emissions from the cooling tower.

Secondary emissions occur when the waste streams, such as the product column bottoms and any unsalable acetonitrile or HCN, are burned in an incinerator (Vent P). Another source of secondary emissions (Q) is the evaporation of organics from the deep-well pond.[4]

2. Process Variations

When HCN and acetonitrile are not recovered for sale, the HCN column, HCN storage, HCN loading, acetonitrile purification column, acetonitrile storage, and acetonitrile loading are eliminated and the light ends plus the crude acetonitrile are sent directly to the incinerator for disposal. As another process variation, only the HCN may be recovered for internal use or for sale. Some variations in the arrangement of the columns in the purification section are also possible.[3,4]

Catalyst 41 is currently used, rather than Catalyst 21, by all domestic acrylonitrile producers. Catalyst 41 reduces the emissions from the absorber vent gas (Vent A).[4] A new acrylonitrile catalyst developed and used by Nitto Chemical Industry Company, Ltd., of Japan (licensed to SOHIO for marketing) achieves high purity and product yield and low by-product yield but is not used in the United States.[1]

C. OTHER PROCESSES

Although acrylonitrile has been produced domestically by the addition of hydrogen cyanide to acetylene, the reaction of propylene with nitric oxide, and the dehydration of ethylene cyanohydrin prepared from ethylene oxide, all domestic plants using these processes have been shut down. The ammoxidation of propane, rather than propylene, has been studied on a pilot scale only and, unless the economics of the process become more favorable, will not likely be widely used.[1,4]

Other processes for the ammoxidation of propylene are used overseas and differ from the SOHIO process mainly in the use of a fixed-bed reactor (except for the Montedison-UOP process, which employs a fluidized-bed catalytic reactor) and a different catalyst system. The catalyst system used by the Montedison-UOP process reportedly reduces the by-products produced and therefore could reduce the emissions from the incinerator. Two plants have been built that use this process but no data are available on the absorber vent emissions.[1,2,7]

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Sections 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation. It should be noted that although ethane is included in VOC emission totals in this report, it does not, based on current research data, participate in ozone-forming reactions to an appreciable extent.

A. SOHIO ACRYLONITRILE PROCESS

1. Model Plant

The model plant* for this study has an acrylonitrile capacity of 180,000 Mg/yr, based on 8760 hr of operation annually.** It also produces 21,600 Mg/yr of hydrogen cyanide (HCN) and 5,000 Mg/yr of acetonitrile as by-products, which are sold or incinerated, depending on the market demand. For this study the model plant incinerates 8640 Mg of HCN and 5,000 Mg of acetonitrile per year because of lack of demand. The SOHIO process for ammoxidation of propylene (Fig. III-1) using catalyst 41 best represents today's acrylonitrile manufacturing and engineering technology. Two reactors and quench neutralizers feeding a single recovery and purification train is typical for plants built recently.[1]

Typical raw material, intermediate, product and by-product storage tank capacities were estimated for a 180,000-Mg/yr plant. Storage tank requirements are given in Sect. IV.A.2.c. Estimates of potential fugitive sources, based on data from existing facilities, are given in Sect. IV.A.2.d. Characteristics of the model plant that are important in air-dispersion modeling are given in Table B-1 in Appendix B.

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*See p I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly production rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. Therefore, from the standpoint of cost effectiveness calculations, the error introduced by assuming continuous operation is negligible.

2. Sources and Emissions

The process emissions estimated for the acrylonitrile model plant are based on emissions reported in response to EPA's requests for information from selected companies, the Du Pont and Vistron trip reports, studies by Houdry and Monsanto for EPA, SRI information, and understanding of the process chemistry and yields. Emission rates and sources for the SOHIO acrylonitrile process are summarized in Table IV-1.

a. Absorber Vent -- The absorber vent gas (Vent A, Figure III-1) contains nitrogen and unreacted oxygen from the air fed to the reactor; propane and unreacted propylene from the propylene feed; and product acrylonitrile, by-product hydrogen cyanide (HCN), acetonitrile, other organics not recovered in the absorber, and some water vapor. Table IV-2 shows the composition of this stream for the model plant. The composition of the absorber vent gas depends on the catalyst, reactor conditions, propylene purity, production rate, and absorber operating conditions. One plant has reported acrylonitrile emissions from their absorber vent that are equivalent to 30 times those from the model plant.[2,3] The acrylonitrile emissions of the model plant are meant to represent typical emissions from a well-designed and operated SOHIO process.[2--6] The propane and propylene emissions are approximately 90% of the volatile organic compounds (VOC) in the vent gas (see Table IV-2). The amount of propane is directly proportional to the amount of propane in the propylene feed, assumed to be 5 wt % for the model plant, since propane is not converted in the reactor.[6]

During startup of a reactor the reactor product by-passes the quench neutralizer and absorber, or the absorber only, for a short period of time. The startup emission rate and composition change during this time. The emissions during startups are estimated in Table IV-1 as yearly averaged values, based on four startups of each of two reactors each year and each startup lasting for 1 hr.

b. Column Vents -- The vent gases from the recovery, acetonitrile, acetonitrile purification, light-ends, HCN, and product columns (Vents B, Fig. III-1) are

Table IV-1. Uncontrolled Emissions of Acrylonitrile and Total VOC from Model Plant Using SOHIO Process

Source	Stream Designation (Fig. III-1)	Emission Ratio (g/kg)[a]		Emission Rate (kg/hr)	
		Acrylonitrile	Total VOC	Acrylonitrile	Total VOC
Absorber vent, normal	A	0.10	100.0	2.05	2050
Absorber vent, startup[b]	A	0.187	0.249	3.84	5.11
Column vents	B	5.00	10.00	103.00	205.00
Storage vents					
Crude acrylonitrile	C	0.048	0.048	0.986	0.986
Acetonitrile			0.021		0.43
Hydrogen cyanide	D		0.041		0.842
Acetonitrile run tanks	F	0.128	0.128	2.62	2.62
Acrylonitrile storage	G	0.531	0.531	10.9	10.9
Handling					
Hydrogen cyanide[c]	H		0.026		0.54
Acetonitrile[c]	J				
Acrylonitrile[c]	K	0.167	0.167	3.44	3.44
Acrylonitrile[d]	L	0.150	0.150	2.16	2.16
Fugitive	N	0.806	1.65	16.6	33.9
Secondary					
Incinerator	P		0.360		7.40
Deep-well pond	Q		13.00		267.00
Total		7.07	126.	146.	2590.

[a] g of emission per kg of acrylonitrile produced.

[b] Average rate for entire year, based on 8 startups per year lasting 1 hour each.

[c] By tank car.

[d] By barge.

Table IV-2. Model-Plant Absorber Vent Gas Composition

Component	Amount (wt %)	Emission Ratio (g/kg)[a]
Acrylonitrile	0.001	0.1
Acetonitrile	0.025	2.0
Hydrogen cyanide	0.002	0.2
Propane	0.759	60.7
Propylene	0.375	30.0
Ethane	0.038	3.0
Other VOC	0.050	4.0
Total VOC	1.250	100.0
Inert gases (N_2, O_2, CO_2, H_2O, CH_4)	97.25	7780.0
Carbon monoxide	1.50	120.0
Total	100.	8000.

[a] g of emission per kg of acrylonitrile produced.

the noncondensibles that are dissolved in the feed to the columns, the VOC that are not condensed, and, for the columns operated under vacuum, the air that leaks into the column and is removed by the vacuum jet systems. An estimate was made on the quantity of these emissions as the available data are scarce and vary widely.[6,7,12]

c. Storage and Handling Emissions -- Emissions result from the storage and handling of acrylonitrile and by-product and intermediate streams. Sources for the model plant are shown in Fig. III-1 (Sources C through L). Storage tank parameters for the model plant are given in Table IV-3. The calculated emissions in Table IV-1 are based on fixed-roof tanks, half full, and an 11°C diurnal temperature variation. Emission equations from AP-42 were used with one modification. The breathing losses were divided by 4 to account for recent evidence that the AP-42 breathing-loss equation overpredicts emissions.[7,8]

Propylene and ammonia are stored in pressure tanks and are not vented. The only emissions are from relief valves,[6] which are covered as fugitive sources in the following section (d). For the model plant both propylene and ammonia are received via pipe lines.

HCN boils at 26°C and is stored in a refrigerated tank at 0°C in the model plant. It may also be stored in a pressure tank, with the vapors condensed by refrigeration at -8 to 0°C. noncondensibles and associated HCN from storage and handling are normally incinerated.[6]

Emissions from loading of acrylonitrile and HCN in railroad tank cars and from loading approximately 45% of the acrylonitrile in barges were calculated by use of the equations from AP-42 and are shown in Table IV-1. The emission from loading acetonitrile is shown as 0 to agree with the assumption that all of the by-product acetonitrile is burned (see Sect. e, "Secondary Emissions"). At least two plants sell some of the by-product acetonitrile produced.[4,5]

d. Fugitive Emissions -- Process pumps, compressors, and valves are potential sources of fugitive emissions. The model plant is estimated to have the following equipment:

Table IV-3. Model-Plant Storage Parameters

Content	Tank Size (m^3)	Turnovers Per Year	Bulk Liquid Temperature (°C)	Vapor Pressure (kPa)
Propylene (4 tanks)	320	345	21	1050
Ammonia (4 tanks)	190	194	21	890
Crude acrylonitrile	2500	6	27	16.4
Acrylonitrile (2 tanks)	380	294	27	16.4
Acrylonitrile (2 tanks)	5680	20	27	16.4
Hydrogen cyanide (2 tanks)	190	83	0	35.2
Acetonitrile	380	61	27	12.9

Pumps in light-liquid service	50
Pipeline valves in gas/vapor service	200
Pipeline valves in light-liquid service	1000
Safety/relief valves in gas/vapor service	80
Compressor seals	2

Half of the pumps, the pipeline valves in both gas/vapor and light-liquid service, and the safety/relief valves handle acrylonitrile. The fugitive-emission factors from Appendix C were applied to this valve and pump and compressor seal count, and the total is shown in Table IV-1 as fugitive emissions.

e. Secondary Emissions -- Secondary VOC emissions can result from the handling and disposal of process-waste liquid streams. Two potential sources (P and Q) are indicated in Fig. III-1 for the model plant.

The emissions from the incinerator (Source P) were estimated on the assumption that all of the product column bottoms (Stream 22) and by-product acetonitrile (Stream 18) goes to the incinerator but that only 40% of the by-product HCN (Stream 26) is incinerated,[3] with the rest being loaded in railroad tank cars; the emissions are shown in Table IV-1.

The emissions from the deep-well pond were estimated from the factors reported[3] by Monsanto Research Corp. for the sampling program performed for EPA, and are shown in Table IV-1.

B. OTHER PROCESSES

No data are available on emissions from other ammoxidation processes or from processes used previously for production of acrylonitrile.

C. REFERENCES*

1. D. A. Olson, "Acrylonitrile," Chemical Engineering Progress 73(11), 42--45 (1977).

2. Responses to EPA requests for information on acrylonitrile emissions; see Appendix E.

3. T. W. Hughes and D. A. Horn, Source Assessment: Acrylonitrile Manufacture (Air Emissions), EPA-600/2-77-107j, Research Triangle Park, NC (September 1977).

4. J. A. Key, IT Enviroscience, Inc. Trip Report to Beaumont Works, E. I. du Pont de Nemours & Co., Beaumont, TX, Sept. 7, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

5. J. A. Key, IT Enviroscience, Inc., Trip Report to Vistron Corp., Lima, OH, Oct. 4, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

6. W. A. Schwartz et al., Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 2: Acrylonitrile Manufacture, EPA-450/3-73-006-b, Research Triangle Park, NC (February 1975).

7. C. C. Masser, "Storage of Petroleum Liquids," p. 4.3-13 in Compilation of Air Pollutant Emission Factors, AP-42, 3d ed., EPA, Research Triangle Park, NC (August 1977).

8. E. C. Pulaski, letter from TRW to Richard Burr (EPA), May 30, 1979.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. SOHIO ACRYLONITRILE PROCESS

1. Absorber Vent

Absorber vent gases can be thermally oxidized to effectively control the acrylonitrile and VOC in them; however, because of the large percentage of nitrogen and other noncombustible gases normally present, supplemental fuel must be added to ensure proper combustion. A portion of this supplemental fuel can be the liquid-organic waste and by-products from the acrylonitrile recovery and purification that are not sold. However, even though the thermal oxidizer is designed to burn all the liquid-organic waste and by-product acetonitrile and HCN produced, additional supplemental fuel is required. A reduction of 99% in acrylonitrile and VOC emissions was used for calculation of the controlled emissions from the model-plant thermal oxidizer that originated in the absorber vent (see Table V-1).[1,2]

Catalytic oxidation can also control the acrylonitrile and VOC emissions from the absorber vent, although significant destruction of the propane in the emissions has not yet been achieved.[3] It is believed that a catalytic system can be developed to destroy propane, as well as the other VOC.[4]

No control has been identified for the emissions from the absorber vent during startup when the vent gases go from air to fuel in a short time. Startup emissions can be minimized by being sent through the absorber before they are vented; this requires an absorber for each reactor.[5,6] The calculated uncontrolled emissions from reactor startup are shown in Table V-1. These emissions reflect a yearly average based on eight reactor startups, each lasting for 1 hr.

2. Column Vents

The emissions from the column vents can be controlled by incineration in a flare or by scrubbing.[1,5] For the model plant a flare with a tip pressure drop of 3 in. of water was selected to provide low back pressure to the columns to

Table V-1. Acrylonitrile and Total VOC Controlled Emissions for Model-Plant Acrylonitrile by SOHIO Process

Source	Stream Designation (Fig. III-2)	Control Device or Technique	Emission Reduction (%)	Emission Ratio (g/kg)[a]		Emission Rate (kg/hr)	
				Acrylonitrile	Total VOC	Acrylonitrile	Total VOC
Absorber vent (normal)	A	Thermal oxidizer	99 (or greater)	0.0010	1.00	0.0205	20.5
(startup)[b]	A			0.187	0.249	3.84	5.11
Column vents	B	Flare	99 (or greater)	0.0500	0.100	1.03	2.05
Storage vents							
Crude acrylonitrile	C	Water scrubber	99	0.00048	0.00048	0.00986	0.00986
Hydrogen cyanide	D	Flare	99 (or greater)	0	0.00041	0	0.00842
Acetonitrile	E	Water scrubber	99	0	0.00021	0	0.0043
Acrylonitrile run tanks	F	Water scrubber	99	0.00128	0.00128	0.0262	0.0262
Acrylonitrile storage	G	Water scrubber	99	0.00531	0.00531	0.109	0.109
Handling							
Hydrogen cyanide[c]	H	Flare	99 (or greater)	0	0.00026	0	0.0054
Acetonitrile[c]	J	Water scrubber	99	0	0	0	0
Acrylonitrile[c]	K	Water scrubber	99	0.0017	0.0017	0.0344	0.0344
Acrylonitrile[d]	L	Water scrubber	99	0.0011	0.0011	0.0216	0.0216
Fugitive	N	Detection and correction of major leaks	71	0.238	0.487	4.88	10.0
Secondary							
Incinerator	P	None	0	0	0.360	0	7.40
Deep-well pond	Q	Lube oil cover	92	0	1.100	0	22.6
Total				0.300	3.31	9.97	67.9

[a] g of emission per kg of acrylonitrile produced.

[b] Average rate for entire year, based on 8 startups per year lasting 1 hour each. No control has been identified for startup emissions.

[c] By tank car.

[d] By barge.

prevent upsets. A reduction of 99%* was used in the calculations of the controlled emissions that originated in the column vents (see Table V-1), based on smokeless operation of the flare and the gas flow to the flare at greater than 10% of the maximum flow.[7]

3. Storage and Handling Sources

Controls for storage and handling emissions from the synthetic organic chemical manufacturing industry are discussed in a separate EPA report.[8] The following controls for the storage and handling emissions from the model plant were selected based on demonstrated use in acrylonitrile plants.[1,3,9--11] Floating-roof tanks are also used in some services to control storage emissions, with a reported reduction of greater than 95%.[5]

a. Crude Acrylonitrile Storage -- Emissions from the model plant crude acrylonitrile storage vents are controlled by water scrubbers. A reduction of 99% was used in the calculations of the controlled emissions from the crude acrylonitrile storage (see Table V-1).

b. Hydrogen Cyanide Storage and Handling -- Emissions from all HCN storage and loading vents in the model plant are controlled by a separate flare. A refrigerated vent condenser can also be used for recovery of HCN from the vent gases before they are sent to the flare.[3]

A reduction of 99%* of the VOC to the flare was used to calculate the controlled emissions resulting from the flaring of HCN storage and loading vent gases (see Table V-1).[7]

c. Acetonitrile Storage and Handling -- Emissions from acetonitrile storage and handling in the model plant are controlled by a water scrubber. A removal efficiency of 99% was used to calculate the controlled emissions from acetonitrile storage and railroad tank-car loading (see Table V-1), based on reported field experience.[3]

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*Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using specific fuels. Efficiencies cited are for tentative comparison purposes.

d. Product Acrylonitrile Storage and Handling -- In order to prevent cross contamination of the product, the model plant has a separate water scrubber for control of emissions from the product acrylonitrile storage and handling. Field experience indicates that a removal efficiency of 99% can be achieved with a water scrubber;[3] this efficiency factor was used for calculation of the controlled emissions from the scrubber.

4. Fugitive-Emission Sources

Controls for fugitive emissions from the synthetic organic chemicals manufacturing industry are discussed in another EPA document.[12] Emissions from pumps and valves can be controlled by an appropriate leak-detection system and repair and maintenance as needed. Controlled fugitive emissions calculated with the factors given in Appendix C are included in Table V-1; these factors are based on the assumption that major leaks are detected and repaired.

5. Secondary Sources

a. Incinerator -- The VOC emissions caused by burning of the liquid-organic waste streams are estimated to be the same when they are burned as a portion of the supplemental fuel to the thermal oxidizer (see Sect. V.A.1.) as when they are burned in the incinerator, and this quantity is shown in Table V-1. No data are available on the emissions caused by burning the liquid-organic wastes in the thermal oxidizer.

b. Deep-Well Pond -- Control on the secondary emissions from the deep-well pond is a layer of lubrication oil on the water. The controlled emissions from the deep-well pond were calculated with the emission factors given by Monsanto in their report on measured emissions.[13]

B. OTHER PROCESSES

Data are not currently available concerning control devices for other ammoxidation processes nor for the previously used processes for production of acrylonitrile.

C. REFERENCES*

1. Responses to EPA requests for information on acrylonitrile emissions; see Appendix E.
2. J. W. Blackburn, IT Enviroscience, Inc., Control Device Evaluation. Thermal Oxidation, (July 1980) (EPA/ESED report, Research Triangle Park, NC).
3. J. A. Key, IT Enviroscience, Inc., Trip Report To Beaumont Works, E. I. du Pont de Nemours & Co., Beaumont, Texas, Sept. 7, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
4. W. R. Chalker, E. I. Du Pont de Nemours & Co., letter dated Feb. 6, 1979, to D. R. Patrick, EPA, with comments on the draft report Acrylonitrile.
5. M. A. Pierle, Monsanto Chemical Intermediates Co., letter dated Mar. 16, 1979, to D. R. Patrick, EPA, with comments on draft report Acrylonitrile.
6. M. A. Pierle, Monsanto Chemical Intermediates Co., letter dated Aug. 10, 1979, to D. C. Mascone, EPA, with information on startup emissions from acrylonitrile plants.
7. V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).
8. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).
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10. Responses to Texas Air Control Board 1975 Emission Inventory Questionnaire; see Appendix E.
11. Responses to Louisiana Air Control Commission 1975 Emission Inventory Questionnaire; see Appendix E.
12. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).
13. T. W. Hughes and D. A. Horn, Source Assessment: Acrylonitrile Manufacture (Air Emissions), EPA-600/2-77-107; Research Triangle Park, NC (September 1977).

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VI. IMPACT ANALYSIS

A. CONTROL COST IMPACT

This section gives estimated costs and cost-effectiveness data for control of acrylonitrile and total VOC emissions resulting from the production of acrylonitrile. Details of the model plant (Fig. III-1) are given in Sects. III and IV. Cost-estimate sample calculations are included in Appendix D.

Capital cost estimates represent the total investment required to purchase and install all equipment and material required to provide a complete emission control system performing as defined for a new plant at a typical location. These estimates do not include the cost of acrylonitrile production lost during installation or startup, research and development, or land acquisition.

Bases for the annual cost estimates for the control alternatives include utilities, operating labor, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. The cost factors used are itemized in Table VI-1.

1. Sohio Acrylonitrile Process

a. Absorber Vent -- The estimated installed capital cost of a thermal oxidizer designed to reduce by 99% or greater the acrylonitrile and total VOC from the adsorber vent is $3,400,000 when recuperative heat recovery is used or is $4,000,000 when the heat is recovered by steam being generated in a waste-heat boiler. These costs are based on a thermal oxidizer that is designed for a residence time of 0.75 sec at 870°C, is completely installed, and is equipped to burn liquid wastes plus supplemental natural-gas fuel. See Appendix D for the cost-estimate sample calculations for a thermal oxidizer, based on a complete installation as described in the control device evaluation report on thermal oxidizers.[1]

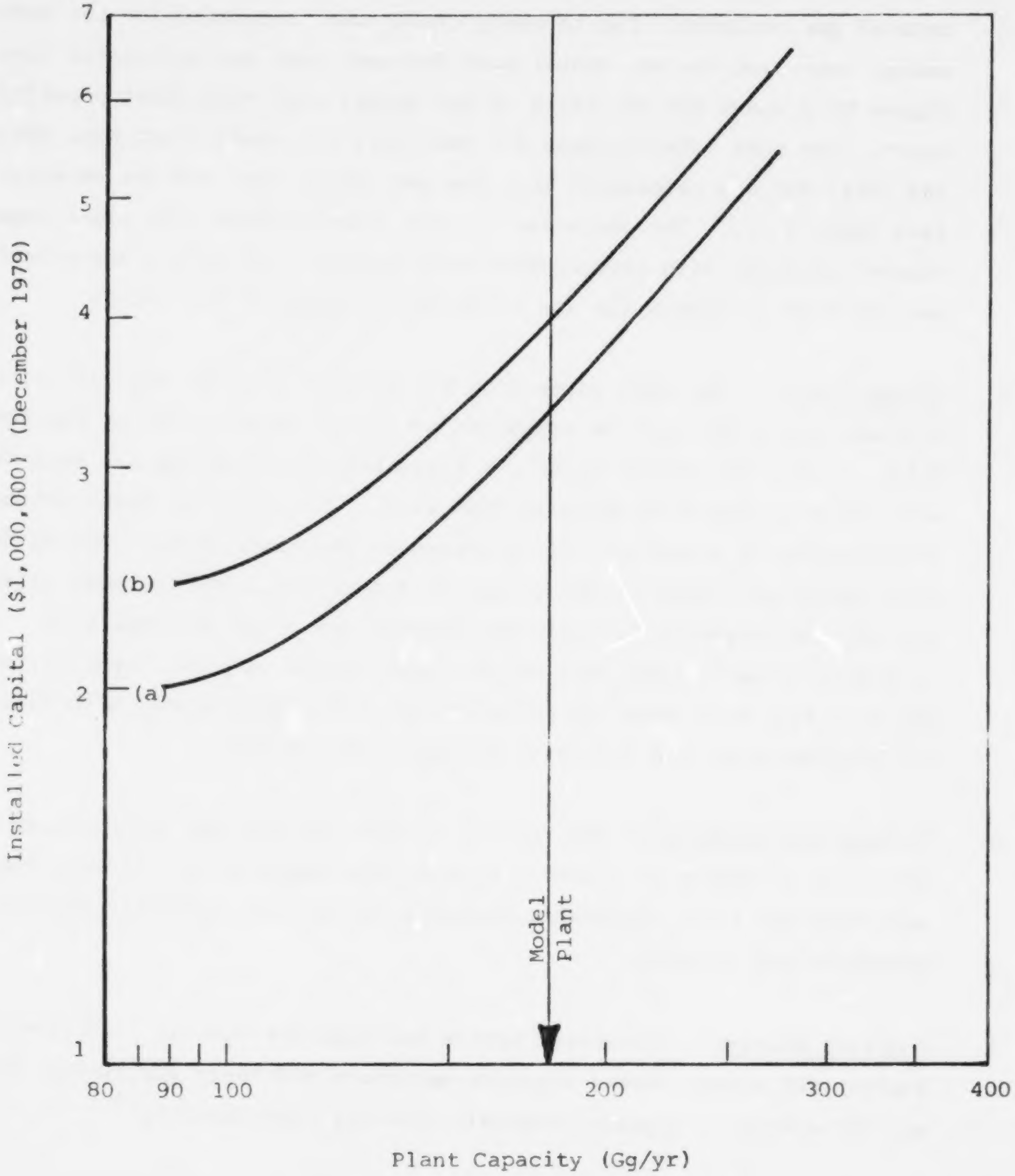
The vent gas rate varies directly with the production rate; therefore a plant with half the capacity of the model plant will require a thermal oxidizer with half the capacity of one for the model plant. Figure VI-1 was plotted to show the variation of installed capital cost of a thermal oxidizer, both with recuperative heat recovery and with a waste-heat boiler, versus plant capacity.

Table VI-1. Annual Cost Parameters

Operating factor	8760 hr/yr[a]
Operating labor	$15/man-hr
Fixed costs	
Maintenance labor plus materials, 6%	29% of installed capital cost
Capital recovery, 18%[b]	
Taxes, insurances, administration charges, 5%	
Utilities	
Process water	$0.07/m^3 ($0.25/thousand gal)
Electric power	$8.33/GJ ($0.03/kWh)
Steam	$5.50/Mg ($2.50/thousand lb or million Btu)
Natural gas	$1.90/GJ ($2.00/thousand ft^3 or million Btu)
Heat recovery credits (equivalent to natural gas)	$1.90/GJ ($2.00/million Btu)

[a] Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

[b] Based on 10-year life and 12% interest.



(a) Thermal oxidizer with recuperative heat recovery
(b) Thermal oxidizer with waste-heat boiler

Fig. VI-1. Installed Capital Cost vs. Plant Capacity for Emission Control (Thermal Oxidation)

To determine the cost effectiveness of the thermal oxidizer, estimates were made of the gross annual operating cost for both recuperative heat recovery and a waste-heat boiler. The liquid wastes were given a value equal to that for the natural gas replaced. The recovery credit was calculated for the waste-heat boiler case, and the net annual cost for each case was calculated (see Table VI-2). Figure VI-2 shows the variation of net annual cost with plant capacity for both cases. The cost effectiveness for each case for controlling both acrylonitrile and total VOC was calculated from the net annual cost and the emission reduction (see Table VI-2). The variation in cost effectiveness with plant capacity of the thermal oxidizer with recuperative heat recovery and with a waste-heat boiler and for both acrylonitrile and total VOC is shown in Fig. VI-3.

b. Column Vents -- The vent gases from the columns (Vent B, Fig. III-1) are controlled by a flare with an estimated installed capital cost of $48,000 (see Table VI-2). The variation of the estimated installed capital cost of the flare with plant capacity is shown in Fig. VI-4. The basis for these estimates is the installation of a complete flare system as described in the control device evaluation report on flares.[2] The estimated annual costs and the cost effectiveness for VOC and acrylonitrile emission control are given in Table VI-2. Figure VI-5 is a plot of net annual cost of the flare system vs plant capacity, and curves a and b of Fig. VI-6 show the variation of cost effectiveness with plant capacity for acrylonitrile and for total VOC emission control.

c. Storage and Handling -- The control systems for storage and handling emissions are water scrubbers or flares. Another EPA report covers storage and handling emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.[3]

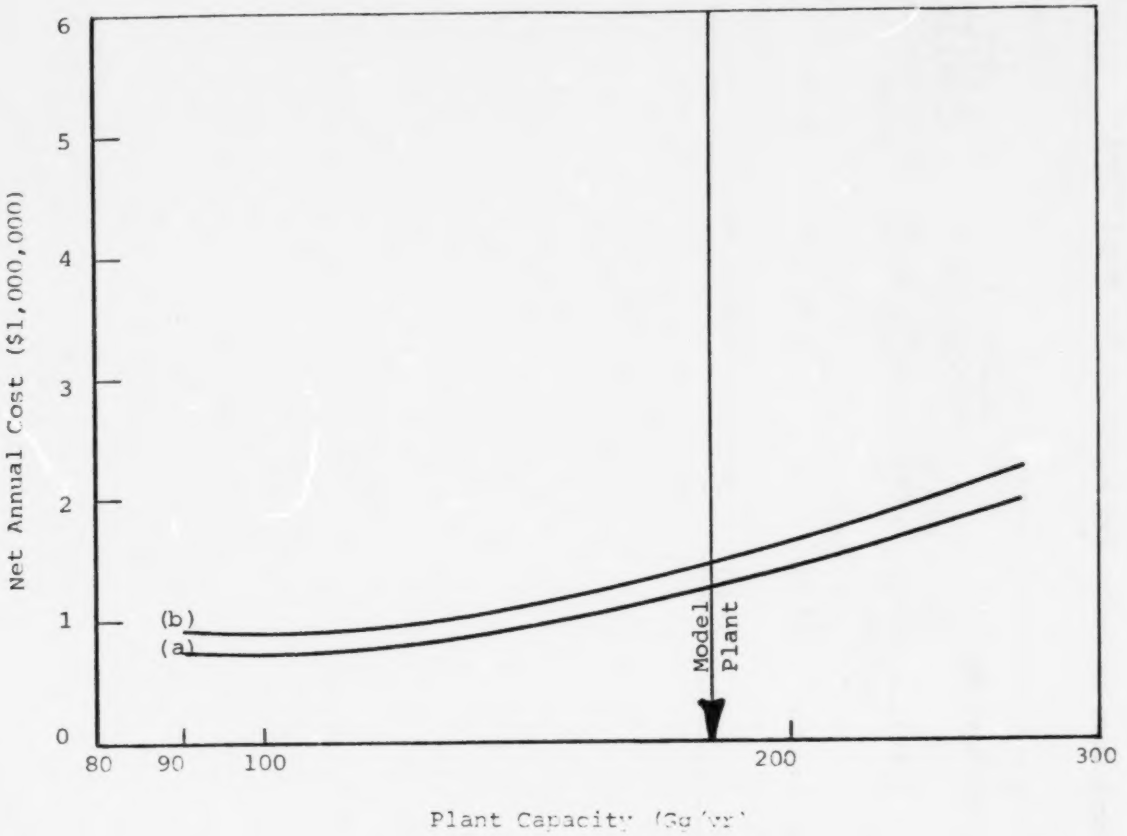
d. Fugitive Sources -- A control system for fugitive sources is defined in Appendix C. Another EPA report covers fugitive emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.[4]

e. Secondary Sources -- No control system has been identified for controlling the secondary emissions from the incinerator. It may be possible to design and operate the thermal oxidizer so that burning the waste organic liquids in it will result in a reduction of secondary emissions, compared with burning them in an older and perhaps less efficient incinerator.

Table VI-2. Emission Control Cost Estimates for Acrylonitrile Model Plant

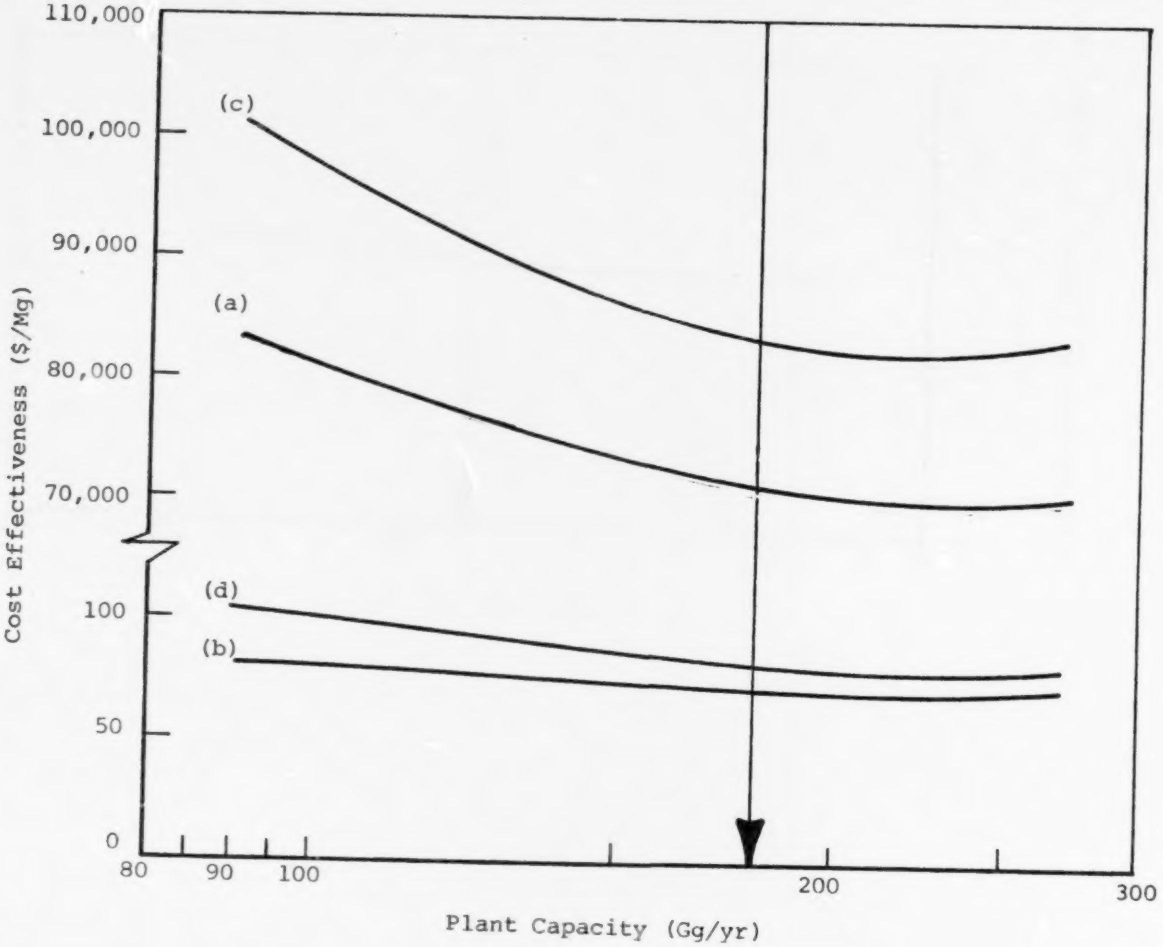
Emission Source	Control Device or Technique	Total Installed Capital Cost	Annual Operating Costs			(B) Emission Reduction			(C) Cost Effectiveness (per Mg)[a]	
			Gross Annual	Recovery Credits	(A) Net Annual	Acrylonitrile (Mg/yr)	Total VOC (Mg/yr)	(%)	Acrylonitrile	Total VOC
Absorber vent	Thermal oxidizer with recuperative heat recovery	$3,400,000	$1,286,000		$1,286,000	18	18,000	99	$71,000	$71
	Thermal oxidizer with waste-heat boiler	4,000,000	5,888,000	4,400,000	1,488,000	18	18,000	99	83,000	83
Column vents	Flare	48,000	24,000		24,000	890	1,800	99	27	13

[a] (C) = (A) ÷ (B).



(a) Thermal oxidizer with recuperative heat recovery
(b) Thermal oxidizer with waste-heat boiler

Fig. VI-2. Net Annual Cost vs. Plant Capacity for Emission Control (Thermal Oxidation)



(a) Thermal oxidizer with recuperative heat recovery, acrylonitrile
(b) Thermal oxidizer with recuperative heat recovery, total VOC
(c) Thermal oxidizer with waste-heat boiler, acrylonitrile
(d) Thermal oxidizer with waste-heat boiler, total VOC

Fig. VI-3. Cost Effectiveness vs. Plant Capacity for Emission Control (Thermal Oxidation)

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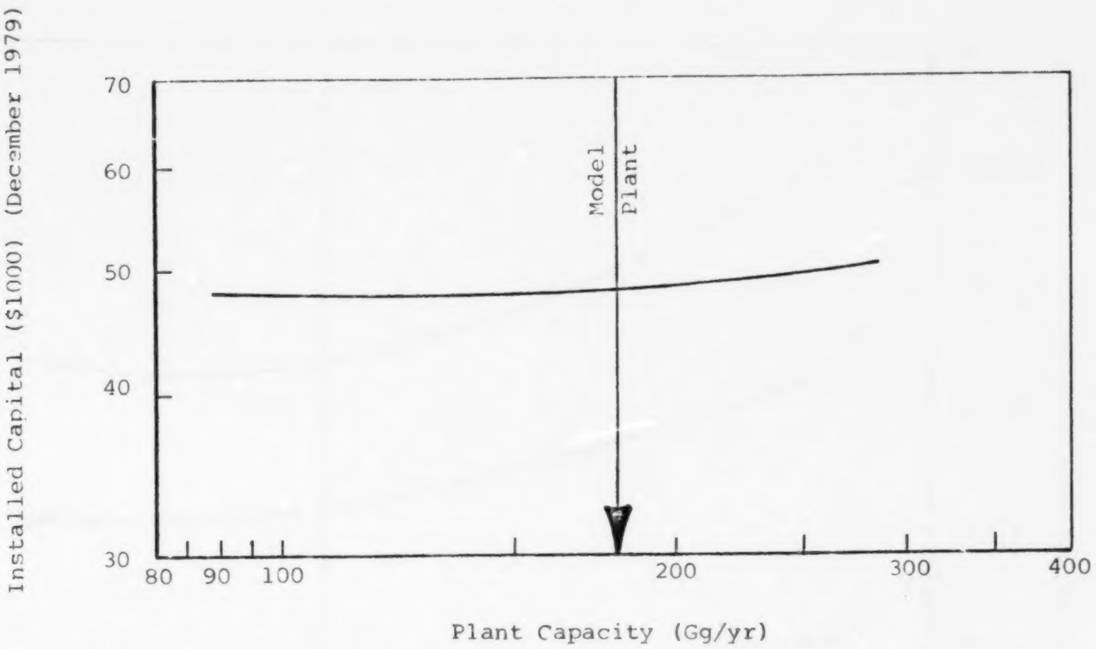

Fig. VI-4. Installed Capital Cost vs. Plant Capacity for Emission Control (Flaring of Column Vent Gases)

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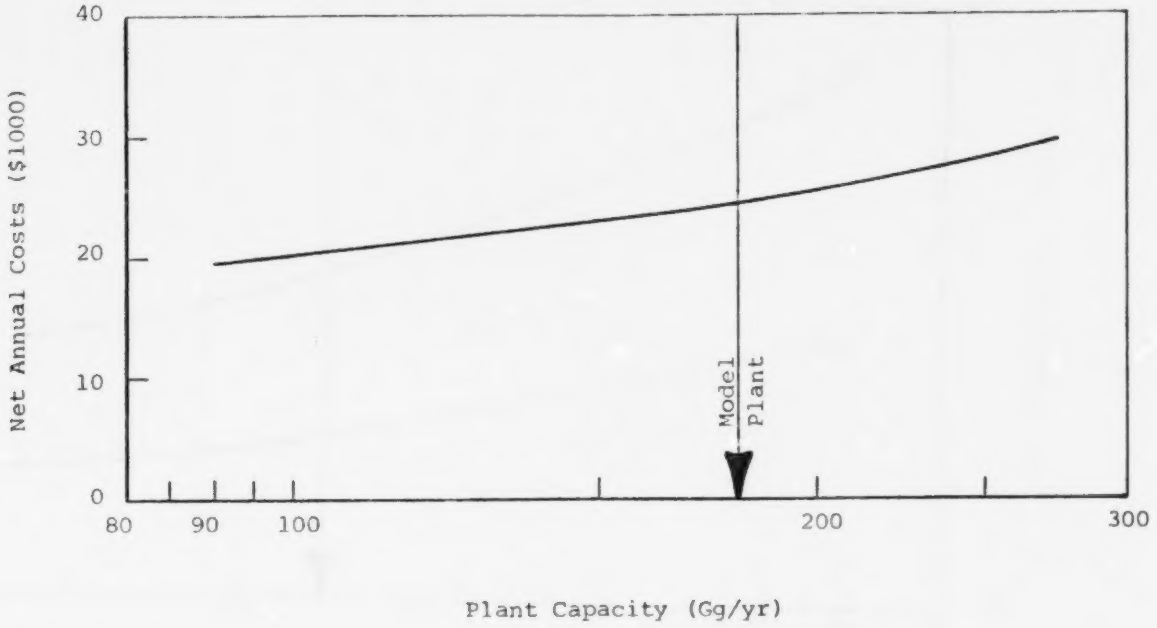
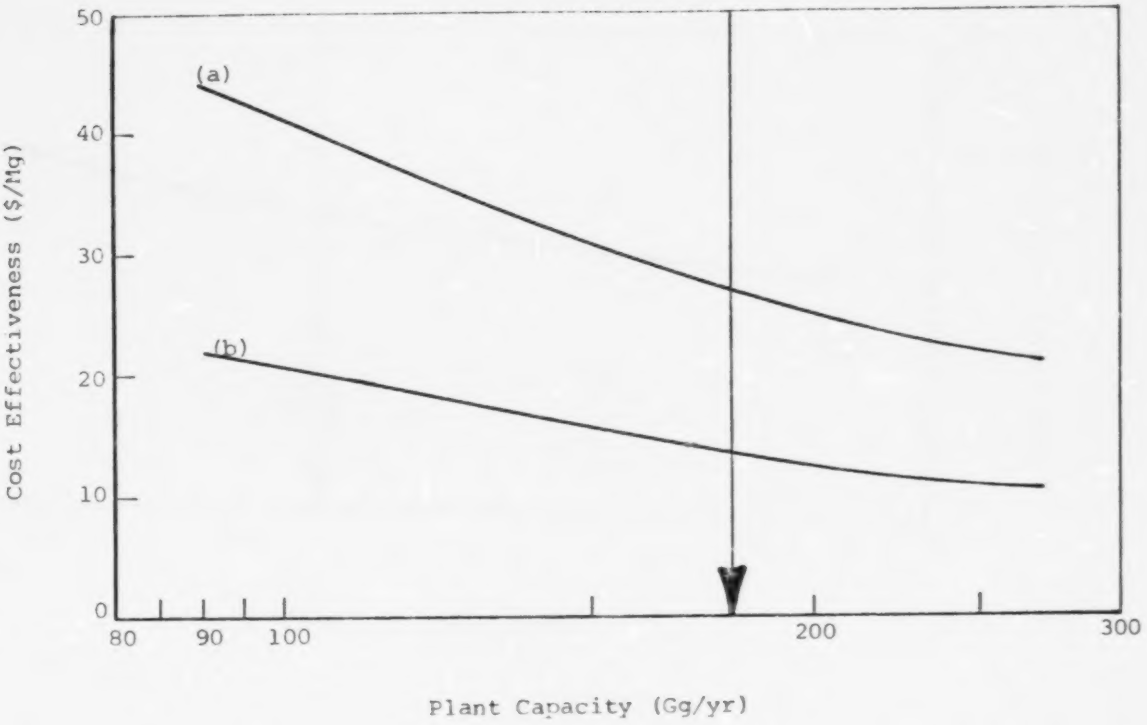


Fig. VI-5. Net Annual Cost vs. Plant Capacity for Emission Control (Flaring of Column Vent Gases)



(a) Acrylonitrile
(b) Total VOC

Fig. VI-6. Cost Effectiveness vs. Plant Capacity for Emission Control (Flaring of Column Vent Gases)

The emissions from the deep-well pond are controlled by means of a layer of oil maintained on the surface. Insufficient data are available at this time to estimate the annual costs or cost effectiveness of this technique.

2. Other Processes

Data are available only for the Sohio process for producing acrylonitrile by the ammoxidation of propylene. No data are available for other processes, which include the addition of hydrogen cyanide to acetylene, the reaction of propylene with nitric acid, the dehydration of ethylene cyanohydrin prepared from ethylene oxide, and the ammoxidation of propane.

B. ENVIRONMENTAL AND ENERGY IMPACTS

1. Sohio Acrylonitrile Process

Table VI-3 shows the environmental impact of reducing acrylonitrile and total VOC emissions by application of the described control systems to the model plant. From an energy standpoint a typical uncontrolled acrylonitrile plant will require only electrical power since enough steam is produced by the process to drive the compressor and meet process steam requirements.[5,6] The electrical power requirements are estimated to be approximately 500 kJ/kg of acrylonitrile. Individual impacts are discussed below.

a. Absorber Vent -- The thermal oxidizer reduces acrylonitrile emissions from the absorber vent by 18 Mg/yr and total VOC emissions by 18,000 Mg/yr for the model plant. The thermal oxidizer uses natural gas as supplemental fuel, steam to atomize the liquid-organic wastes, and electric power for the blowers, lighting, and instruments. The total energy required to operate the thermal oxidizer is approximately 59 GJ/hr when recuperative heat recovery is used and is 320 GJ/hr when the heat is recovered by steam being generated in a waste-heat boiler. The liquid organic wastes supply about 42 GJ/hr of the total energy for both cases. For the waste-heat boiler case the steam produced is equivalent to about 260 GJ/hr.

b. Column Vents -- The flare system reduces acrylonitrile by 890 Mg/yr and total VOC from these sources by 1800 Mg/yr for the model plant. Generation of NO_x, CO, and smoke from flaring these emissions can have a negative impact on the environment if steam injection is not controlled carefully to ensure complete combustion.

Table VI-3. Environmental Impact of Controlled Model Plant

Source	Stream No. (Fig. III-2)	Control Device or Technique	Emission Reduction (%)	Emission Reduction (Mg/yr)	
				Acrylonitrile	Total VOC
• Absorber vent					
Normal	A	Thermal oxidizer	99 (or greater)	18	18,000
Startup	A	None			
Column vents	B	Flare	99 (or greater)	890	1,800
Storage vents					
Crude acrylonitrile	C	Water scrubber	99	8.6	8.6
Hydrogen cyanide	D	Flare	99 (or greater)		7.3
Acetonitrile	E	Water scrubber	99		3.7
Acrylonitrile run tanks	F	Water scrubber	99	23.	23.
Acrylonitrile storage	G	Water scrubber	99	95.	95.
Handling					
Hydrogen cyanide[a]	H	Flare	99 (or greater)		4.7
Acetonitrile[a]	J	Water scrubber	99		
Acrylonitrile[a]	K	Water scrubber	99	30.	30.
Acrylonitrile[b]	L	Water scrubber	99	19.	19.
Fugitive	N	Detection and correction of major leaks	71	100.	210.
Secondary					
Incinerator	P	None			
Deep-well pond	Q	Lube oil cover	92		2,100
Total				1200.00	22,000

[a] By tank car.

[b] By barge.

Natural gas is required for the pilot lights, and steam is used to ensure smokeless operation; the total energy required is approximately 500 MJ/hr. The electrical energy required for the flare system instruments and controls is negligible.

c. Other Emissions (Storage and Handling, Fugitive and Secondary) -- Control methods described for these sources are water scrubbers and a flare for storage and handling emissions, correction of major leaks for fugitive emissions, and maintenance of a lubricating oil cover on the deep-well pond for secondary emissions.

Application of these systems results in an acrylonitrile reduction of 280 Mg/yr and a VOC reduction of 2500 Mg/yr for the model plant.

The use of a lubricating oil cover on the deep-well pond for emission control does not consume energy and has no adverse environmental or energy impacts.

2. Other Processes

Emission control systems for other acrylonitrile processes have not been described.

C. REFERENCES*

1. J. W. Blackburn, IT Enviroscience, Inc., Control Device Evaluation. Thermal Oxidation, (July 1980) (EPA/ESED report, Research Triangle Park, NC).

2. V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).

3. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

4. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc. Fugitive Emissions (September 1980) (EPA/ESED report, Research Triancle Park, NC).

5. P. R. Pujado, B. V. Vora, and A. P. Krueding, "Newest Acrylonitrile Process," Hydrocarbon Processing 56(5), 169--172 (1977).

6. W. A. Schwartz et al, Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 2: Acrylonitrile Manufacture, EPA-450/3-73-006-b, Research Triangle Park, NC (February 1975).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

Acrylonitrile is produced in the United States exclusively by the ammoxidation of propylene by the SOHIO process. Processes in which other raw materials are used are no longer in operation, and any new capacity will probably be based on the ammoxidation of propylene process.[1--3]

The annual growth rate of acrylonitrile production is estimated to be 8%. The domestic acrylonitrile capacity available in 1977 will be sufficient to meet the growth rate through 1980. No shortage of either propylene or ammonia is expected during this period.[2]

Emission sources and uncontrolled and controlled emission rates for the model plant are given in Table VII-1. The current emissions projected for the domestic acrylonitrile industry based on the estimated degree of control existing in 1980 are 1080 Mg/yr for acrylonitrile and 56,700 Mg/yr for total VOC. These emission estimates were based on engineering judgement and data from individual acrylonitrile producers, state and local emission control agencies, and the open literature. The following individual estimated projections were made:

	1980 Emissions (Mg/yr)	
Source	Acrylonitrile	VOC
Process	230	51,000
Storage and handling	650	700
Fugitive	200	400
Secondary	0	4,600
Totals	1080	56,700

The predominant emission points are the absorber vent and the column vents. Emissions from the absorber vent were estimated assuming 5% propane in the propylene fed to the reactor. Because propane passes through unreacted, the purity of

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[1] J. L. Blackford, "Acrylonitrile," pp. 607.5032B--607.5032D in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (May 1978).

[2] D. A. Olson, "Acrylonitrile," Chemical Engineering Progress 73(11), 42--45 (1977).

[3] P. R. Pujado, B. V. Vora, and A. P. Krueding, "Newest Acrylonitrile Process," Hydrocarbon Processing 56(5), 169--172 (1977).

Table VII-1. Emission Summary Model Plant

Emission Source	Emission Rate (kg/hr)			
	Uncontrolled		Controlled	
	Acrylonitrile	VOC	Acrylonitrile	VOC
Absorber vent				
Normal	2.05	2050	0.0205	20.5
Startup	3.84	5.11	3.84	5.11
Column vents	103	205	1.03	2.05
Storage vents				
Crude acrylonitrile	0.986	0.986	0.00986	0.00986
Hydrogen cayanide		0.842		0.00842
Acetonitrile		0.43		0.0043
Acrylonitrile run tanks	2.62	2.62	0.0262	0.0262
Acrylonitrile storage	10.9	10.9	0.109	0.109
Handling				
Hydrogen cyanide		0.54		0.0054
Acetonitrile				
Acrylonitrile	3.44	3.44	0.0344	0.0344
Acrylonitrile	2.16	2.16	0.0216	0.216
Fugitive	16.6	33.9	4.88	10.0
Secondary				
Incinerator		7.40		7.40
Deep-well pond	—	267	—	22.6
Total	146	2590	9.97	67.9

the propylene has a signficant effect on the quantity of VOC out the absorber vent. The vent gases from the absorber vent can be controlled by a thermal oxidizer, which will reduce both the acrylonitrile and total VOC emissions by 99% or greater. The installed cost of a thermal oxidizer for the model plant is \$3.4 million with recuperative heat recovery and is \$4.0 million with heat recovery by use of a waste-heat boiler. Supplemental fuel is required and liquid-organic waste can be burned in the thermal oxidizer to supply a portion of the supplemental fuel needed. The cost effectiveness for acrylonitrile is \$71,000/Mg controlled and for total VOC is \$71/Mg if recuperative heat recovery is installed. With heat recovery by use of a waste-heat boiler the cost effectiveness for acrylonitrile is \$83,000/Mg or \$83/Mg for total VOC.

Emissions from storage and handling vents can be controlled by water scrubbers for acrylonitrile and acetonitrile and by sending HCN to the flare system.

Secondary emissions from the deep-well pond are significant but can be controlled by maintaining a lubricating oil layer on the surface of the pond, reducing the VOC emissions by 92%.

APPENDIX A

Table A-1. Physical Properties of Acrylonitrile*

Synonyms	2-Propenenitrile, vinyl cyanide
Molecular fomula	C_3H_3N
Molecular weight	53.06
Physical state	Liquid
Vapor pressure	113.8 mm Hg at 25°C
Vapor specific gravity	1.83
Boiling point	77.5°C
Melting point	-83 to -84°C
Density	0.8060 g/ml at 20°C/4°C
Water solubility	7.3 wt % at 70°C

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*J. Dorigan *et al*, "Acrylonitrile," p. AI-40 in *Scoring of Organic Air Pollants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C)*, MTR-7248, Rev 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

Table A-2. Physical Properties of Acetonitrile*

Synonyms	Methyl cyanide, ethanenitrile, cyanomethane, ethyl nitrile, methane carbonitrile
Molecular fomula	C_2H_3N
Molecular weight	41.05
Physical state	Liquid
Vapor pressure	92.8 mm Hg at 25°C
Vapor specific gravity	1.42
Boiling point	81.6°C
Melting point	-45.72°C
Density	0.786 g/ml at 20°C/20°C
Water solubility	Infinite

*J. Dorigan *et al.*, "Acetonitrile," p. AI-24 in *Scoring of Organic Air Pollutants, Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C)*, MTR-7248, Rev 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

Table A-3. Physical Properties of Hydrogen Cyanide*

Synonyms	Prussic acid
Molecular formula	CHN
Molecular weight	27.03
Physical state	Liquid
Vapor pressure	739.36 mm Hg at 25°C
Vapor specific gravity	0.932
Boiling point	25.7°C
Melting point	-13.3°C
Density	0.6876 ay 20°C/4°C
Water solubility	Infinite

*J. Dorigax et al., "Hydrogen Cyanide," p A III-54 in Scoring of Organic Air Pollutants, Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F-N), MTR-7248, Rev 1, Appendix III, MITRE Corp., McLean, VA (September 1976).

Table B-1. Air-Dispersion Parameters for Model Plant with a Capacity of 180,000 Mg/yr

Source	Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
Absorber vent (uncontrolled)	0.57 (acrylonitrile)	60	1.0	280	40	49
	570 (total VOC)					
Column vents[a] (uncontrolled)	28.5 (acrylonitrile)	60	0.1	Ambient	0.12	15.8
	57.1 (total VOC)					
Thermal oxidizer[b]	0.0057 (acrylonitrile)	18	4.5	533	160	10
	7.76 (total VOC)					
Flare (on column vents)	0.29 (acrylonitrile)	60	0.06	1250		
	0.57 (total VOC)					
Storage and handling (uncontrolled)						
Crude acrylonitrile	0.27	12.2	16.2	Ambient		
Hydrogen cyanide	0.23	7.3	6.1	273		
Acetonitrile	0.12	9.8	7.0	Ambient		
Acrylonitrile run (2)	0.36 (each)	9.8	7.0	Ambient		
Acrylonitrile storage (2)	1.52 (each)	12.2	24.4	Ambient		
Hydrogen cyanide loading	0.15	4.0		Ambient		
Acetonitrile loading	0	4.0		Ambient		
Acrylonitrile rail loading	0.95	4.0		Ambient		
Acrylonitrile barge loading	0.60	2.0		Ambient		
Storage and handling (controlled)						
Crude acrylonitrile scrubber	0.0027	6.0	0.1	Ambient	0.0015	0.19
Acetonitrile scrubber	0.0012	6.0	0.1	Ambient	0.00075	0.086
Acrylonitrile scrubber	0.053	6.0	0.2	Ambient	0.024	0.75
Flare (on hydrogen cyanide)	0.0038	60	0.5	1250		
Fugitive emissions[c] (uncontrolled)	4.6 (acrylonitrile)					
	9.4 (total VOC)					
Fugitive emissions[c] (controlled)	1.4 (acrylonitrile)					
	2.8 (total VOC)					
Secondary emissions						
Incinerator (uncontrolled)	2.1	30	4.5	1140	33	2.08
Deep-well pond (uncontrolled)	74	1.0	60 X 90	Ambient		
Deep-well pond (controlled)	6.3	1.0	60 X 90	Ambient		

[a] Column vent gases (controlled) are released through the flare.

[b] Emissions from the thermal oxidizer include the emissions from burning the liquid-organic wastes that are burned in the liquid waste incinerator of the uncontrolled plant.

[c] Fugitive emissions are evenly distributed over a rectangular area of 50 by 200 m.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

COST ESTIMATE DETAILS

This appendix contains sample calculations showing how the costs presented in this report were estimated.

The accuracy of an estimate is a function of the degree of data available when the estimate was made. Figure D-1 illustrates this relationship. The contingency allowance indicated is included in the estimated costs to cover the undefined scope of the project.

Capital costs given in this report are based on a screening study, as indicated by Fig. D-1, based on general design criteria, block flowsheets, approximate material balances, and data on general equipment requirements. These costs have an accuracy range of +30% to -23%, depending on the reliability of the data, and provide an acceptable basis to determine the most cost-effective alternative within the limits of accuracy indicated.

A. THERMAL OXIDIZER CONTROLLING EMISSIONS FROM MODEL-PLANT ABSORBER VENT

This example is based on the estimated emissions of 80,000 scfm, with a heat content of 25 Btu/scf going to a thermal oxidizer operated at 1600°F with 0.75-sec residence time and equipped with recuperative heat recovery. The estimated emissions include the vent gases from the absorber vent and have the composition shown in Table IV-2. Liquid organic wastes are used as part of the supplemental fuel and supply an average of 40.3 million Btu/hr. Appendix B of the Control Device Evaluation. Thermal Oxidation report[1] was used to estimate the costs as follows. On p B-20 are costs for thermal oxidizers with a residence time of 0.75 sec and with 50% heat recovery by recuperative heat exchange and operating at 1600°F on off-gas with a heat content of 20 Btu/scf. The fuel costs for this case are slightly more than for the case for an off-gas with a heat content of 25 Btu/scf. Since part of the supplemental fuel is the liquid-organic waste from the acrylonitrile process, the utility costs are adjusted to account for the heat supplied by the combustion of the liquid-organic wastes:

$$40.3 \text{ million Btu/hr} \times 8760 \times \frac{\$2.00}{\text{million Btu}} = \$707{,}000/\text{yr}.$$

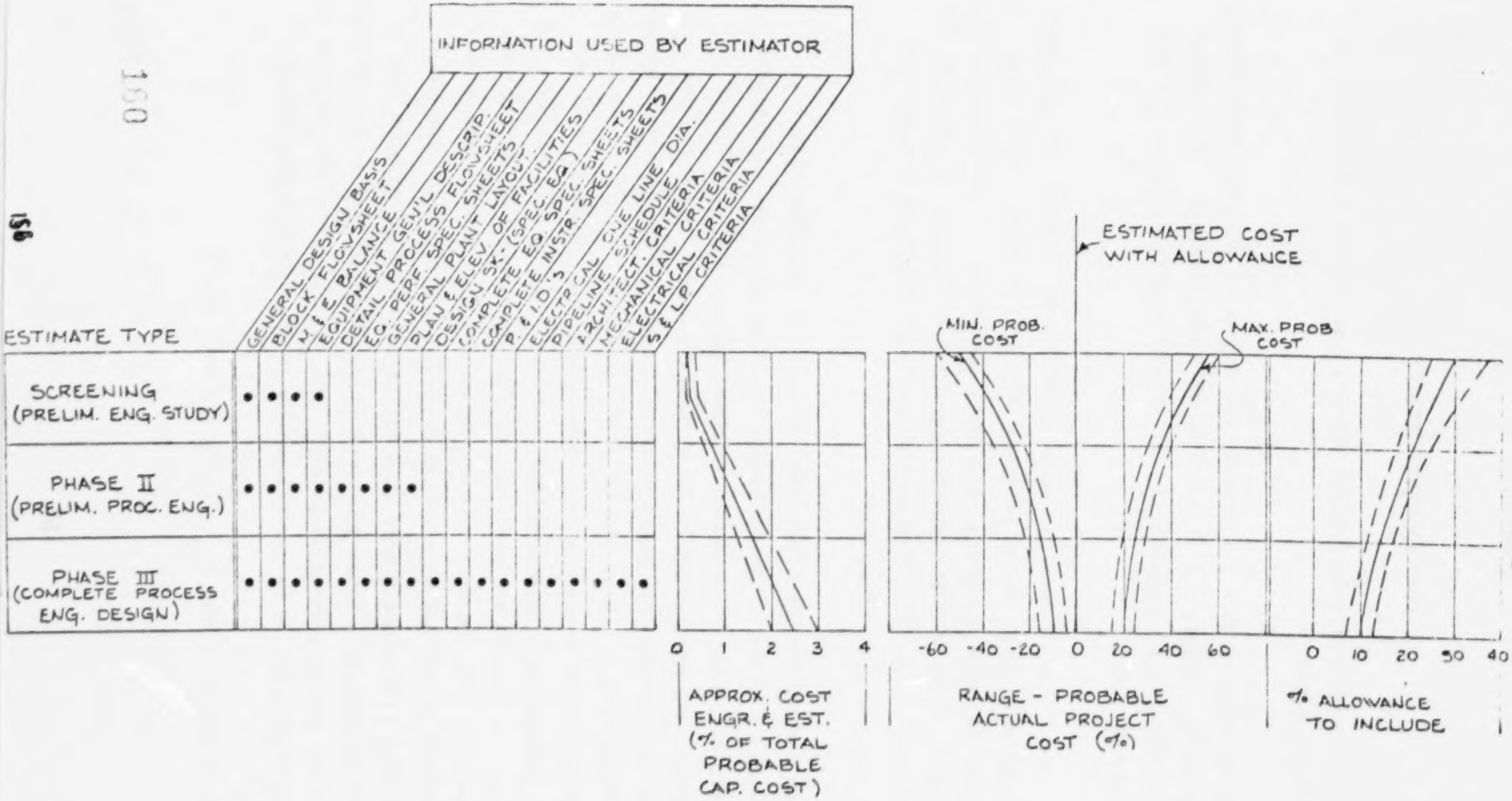

Fig. D-1. Precision of Capital Cost Estimates

Since the costs are given for 50,000 and 100,000 scfm, it is necessary to estimate the costs for 80,000 scfm by interpolation. This was done by plotting the costs versus the scfm on log-log graph paper and reading the costs for 80,000 scfm from the curve:

Total installed capital cost = \$3,400,000
Fixed costs = 986,000
Utilities costs = 980,000
Credit for liquid-organic wastes = (-707,000)
Manpower costs = 27,000
Gross annual operating cost = \$1,286,000

From Table VI-1 of this report:

Emission reduction = 18 Mg of acrylonitrile/yr
= 18,000 Mg of VOC/yr

Cost effectiveness $= \frac{\$1,286,000}{18} = \$71,000$/Mg of acrylonitrile

$= \frac{\$1,286,000}{18,000} = \$71$/Mg of VOC

B. FLARE ON COLUMN VENT EMISSIONS

This example is based on an estimated average emission from the column vents of 1360 lb/hr at 100°F with a molecular weight of 34.

1. Installed Capital Cost

The equation given in Sect. A of Appendix A of the flare report[2] was used to calculate the flare-tip diameter (2.94 in.) that would have a pressure drop of 3 in. H_2O when the vent gases are flared as described above at 1360 lb/hr. Figure B-1 in Appendix B of the flare report shows that the installed capital cost of a total flare system of that size is \$48,000.

2. Gross Annual Operating Cost

From Table VI-1 of this report the total fixed costs, including capital recovery, are 29% of the installed capital cost:

$$\$48,000 \times 0.29 = \$14,000/\text{yr}.$$

From Fig. IV-4 of the flare report[2] the natural gas used for the pilot lights is 60 scfh and for purging is 3 scfh. From Table VI-1 the cost of gas is $2.00 per thousand ft^3:

$$(60 + 3) \times 8760 \times \frac{2.00}{1000} = \$1100/\text{yr}.$$

From Sect. IV-A-1 of the flare report[2] it is estimated that 0.3 lb of steam is required per pound of emission; from Table VI-1 the cost of steam is $2.50/thousand lb. The average emission is 1360 lb/hr:

$$0.3 \times 1360 \times 8760 \times \frac{2.50}{1000} = \$8900/\text{yr}.$$

The annual cost summary is as follows:

Fixed	$14,000
Natural gas	1,100
Steam	8,900
Total	$24,000

3. Cost Effectiveness

Cost effectiveness is the gross annual operating cost, $24,000, divided by the annual VOC or acrylonitrile destroyed at 99% efficiency. From Table VI-3 of this report the total VOC reduction for the column vents is 1800 Mg/yr, and the total acrylonitrile destroyed is 890 Mg/yr:

$$\frac{\$24,000}{1,800} = \$13/\text{Mg of VOC destroyed}.$$

$$\frac{\$24,000}{890} = \$27/\text{Mg of acrylonitrile destroyed}.$$

C. REFERENCES*

1. J. W. Blackburn, IT Enviroscience, Inc., Control Device Evaluation. Thermal Oxidation (July 1980) (EPA/ESED report, Research Triangle Park, NC).

2. V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX E

LIST OF EPA INFORMATION SOURCES

C. P. Priesing, American Cyanamid Company, letter to EPA, Feb. 1, 1978.

Donald W. Smith, E. I. du Pont de Nemours & Co., letter to EPA, Jan. 17, 1978.

Harry M. Keating, Monsanto Chemical Intermediates Co., letter to Hydroscience, Dec. 16, 1977 (nonconfidential parts).

V. E. Stilwell, Louisiana Air Control Commission Emissions Inventory Questionnaire for American Cyanamid Company, Mar. 26, 1976.

H. L. Dey, Texas Air Control Board 1975 Emissions Inventory Questionnaire for E. I. du Pont de Nemours & Company Beaumont Works (nd).

W. E. Elting, Memphis and Shelby County Air Pollution Control Permit Application for E. I. du Pont de Nemours & Co. Memphis Plant (nd).

V. E. Stillwell, EPA Questionnaire for American Cyanamid Company, July 25, 1972.

W. R. Chalker, EPA Questionnaire for E. I du Pont de Nemours & Co., Sept. 18, 1972.

Harry M. Walker, EPA Questionnaire for Monsanto Company, Apr. 28, 1972.

G. K. Doss, EPA Questionnaire for Vistron Corporation, June 13, 1972.

APPENDIX F

EXISTING PLANT CONSIDERATIONS

A. EXISTING PLANT CHARACTERIZATION

Table F-1[1—11] lists emission control devices reported to be in use by industry. To gather information for the preparation of this report two site visits were made to manufacturers of acrylonitrile. Trip reports have been cleared by the companies concerned and are on file at EPA, ESED, in Durham, NC;[3,10] EPA also has received letters in response to requests for information on air emissions from acrylonitrile plant and in response to requests for comments on the draft version of this report. Some of the pertinent information concerning process emissions from existing acrylonitrile plants is presented in this appendix. All six domestic acrylonitrile plants use the Sohio process and catalyst* and employ multiple fluid bed reactors.

1. Du Pont - Beaumont, TX

The process was licensed from Sohio and the plant designed and constructed by Badger, with startup taking place during 1970. A catalytic oxidizer that was installed later to abate emissions from the absorber vent came onstream during September 1976. Table F-2 gives data on the controlled emissions from the catalytic oxidizer. Although the propane destruction efficiency in this unit is only 24%, Du Pont believes that a catalytic oxidation system could have been developed to destroy both propylene and propane.[3,5]

The emissions from the column vents are collected by the flare header system and controlled by a 16-in. flare designed for emergency and shutdown use.

A separate 6-in. flare is used to control emissions from HCN storage and tank-car loading. The HCN storage tanks are refrigerated to 41°F and have a refrigerated vent condenser that vents to the HCN flare.

The storage tanks for crude acrylonitrile, product acrylonitrile, product analysis, and acetonitrile are blanketed with nitrogen under pressure control.

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*Although Catalyst 41 is believed to be currently used, Sohio (Vistron) began marketing a fourth-generation catalyst (Catalyst 49) during 1978 that is more selective than Catalyst 41.[11]

Table F-1. Control Devices Currently Used by the U.S. Acrylonitrile Industry[a]

Company	Control Devices at Various Emission Points			
	Absorber Vent	Column Vents	Storage Tank Vents	Deep-Well Pond
Cyanamid	None	Flare	Scrubbers[b]	Lube-oil cover
Du Pont				
Beaumont, TX	Catalytic oxidizer	Flare	Scrubbers, refrigerated condenser, and flare	Lube-oil cover
Memphis, TN	None	Not reported	Scrubber[b]	Not used
Monsanto				
Alvin, TX	Thermal oxidizer	Flare and vent condenser	Not reported	Lub-oil cover
Texas City, TX	Thermal oxidizer	Water scrubber and flare	Water scrubber, vent condenser, and floating roof	Closed surface system with water scrubber
Vistron	None	Flare	Flare[b]	Lube-oil cover

[a] See refs 1—11.

[b] Some vents go directly to the atmosphere from conservation vents.

Table F-2. Emissions from Catalytic Oxidizers--
Du Pont Beaumont Acrylonitrile Plant[a]

Component	Emission Composition or Flow
Nitriles	0.005 wt %
Other VOC	0.402 wt %[b]
Carbon monoxide	0.227 wt %
VOC flow	1130 kg/hr[b]
Total flow	277 Mg/hr

[a] See ref 3.

[b] 85% of VOC is propane. Propane is considered as having low photochemical reactivity and the catalytic oxidizers were not designed to control propane; see refs 3 and 5.

Conservation/emergency vent valves are piped to water scrubbers that reportedly remove 99.9% of the VOC in the nitrogen released from the tanks before it is emitted to the atmosphere. The water from the scrubbers serving the tanks containing acrylonitrile is recycled to the process. The scrubber water from the scrubber on the acetonitrile tanks goes to a deep well. The scrubber for the product analysis tanks also is used to control the emissions caused by loading railroad tank cars with acrylonitrile. Emissions from loading of acetonitrile are controlled by the scrubber for the acetonitrile storage tank.[3,5]

2. Monsanto - Alvin, TX, and Texas City, TX

The VOC emissions from the absorber vents are controlled by thermal oxidizers at both Monsanto plants during normal operation (see Table F-1). During startup, plants with two or more reactors connected to the same absorber vent the reactor effluent to the atmosphere, without it going through the absorber, to prevent the creation of a flammable mixture in the absorber. The Monsanto Texas City plant has an absorber for each reactor, and during startup the reactor effluent is vented to the atmosphere after passing through the absorber, where some of the VOC is removed.[12]

Data on emissions from the thermal oxidizers used at Monsanto's Chocolate Bayou Plant at Alvin, TX, are given in Table F-3. These thermal oxidizers control the emissions from the absorber vents and also destroy the liquid-waste acetonitrile, the liquid-waste hydrogen cyanide, and the product column bottoms.[6]

Monsanto reports that normal uncontrolled emissions from the absorber contain approximately 2 g of acrylonitrile per kg of acrylonitrile produced. They estimate that the emissions from the column vents contain 0.19 g of acrylonitrile and 1.08 g of VOC per kg of acrylonitrile produced.[9]

Monsanto states that a water scrubber designed to remove 99% of the acrylonitrile emitted from a storage tank requires a blower and refrigerated water and that the scrubber water cannot be recycled to the process but is sent to a stripper for removal of VOC and then recycled to the scrubber. They report that the emissions from the storage tank vents at the Texas City plant are controlled by a water scrubber, vent condenser, or floating roof.[9]

Table F-3. Emissions from Thermal Oxidizers--Monsanto Chocolate Bayou Acrylonitrile Plant[a]

	Emission Composition or Flow			
	First Unit		Second Unit	
Component	5-Sample Average	1 Sample	7-Sample Average	1 Sample
Nitriles	<3.0 ppmv	<3.0 ppmv	<3.0 ppmv	<3.0 ppmv
Other VOC	23.7 ppmv	22.0 ppmv	44.6 ppmv	18.0 ppmv
Methane	0.5 ppmv	0.5 ppmv	0.5 ppmv	0.5 ppmv
Carbon monoxide	74.0 ppmv	89.1 ppmv	88.6 ppmv	90.9 ppmv
Nitrogen oxides	8.0 ppmv[b,c]	Not sampled	∿200 ppmv[b]	Not sampled
VOC flow	3.7 kg/hr	4.0 kg/hr	7.4 kg/hr	3.4 kg/hr
Total flow	151 Mg/hr	181 Mg/hr	163 Mg/hr	182 Mg/hr

[a] Separate identical thermal oxidizers for each of two separate acrylonitrile production units. Samples taken during steady-state operation. See ref 6.

[b] Two samples only.

[c] Probably erroneous analysis per Monsanto.

3. Vistron - Lima, OH[10]

The Vistron Corporation is a subsidiary of the Standard Oil Company (Ohio) and operates acrylonitrile production facilities located adjacent to the Sohio refinery near Lima, OH, to produce acrylonitrile from propylene and ammonia by the Sohio process. The plant was built by Badger in 1965, and there have been no major modifications since 1971. An older plant at the same site is no longer producing acrylonitrile.

The emission control systems described below are those in use in 1977. Vistron is working toward reducing the emissions from its acrylonitrile plant in the future. Emissions vented from the columns are controlled by flaring. A header runs throughout the plant for the purpose of collecting vent gases from the various equipment vents and natural gas from purge applications. From the header the gases pass through a liquid knockout pot and travel up a flare stack. Normal flows to the incinerators will also divert to the flare stack in the event of an incinerator shutdown. The stack consists of a 24-in. pipe extending 200 ft above grade.

Three product tanks, three rundown tanks, and two crude tanks are used; each is equipped with a combination pressure-vacuum relief valve set to relieve to atmosphere at a pressure of 4 in. H_2O or a vacuum of 1 in. H_2O. Nitrogen is fed to the three product tanks and escapes through the pressure-vacuum relief valve to the atmosphere when the pressure exceeds the setting. The new product tank has a continuous nitrogen purge, and the nitrogen to the east and west product tanks is fed through a pressure regulator set to maintain a minimum pressure of 2 in. H_2O. The HCN is stored in horizontal pressure tanks that have a totally contained vent system. The normal vent is directed to either the flare stack or the incinerators. The gases from an emergency vent from each tank go directly to the flare stack through a separate line. A rupture disk designed to burst at 15 psig keeps the emergency vents closed under normal conditions. Both the normal vents and the emergency vents are continually purged with nitrogen.

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

An acrylonitrile plant will generate an excess of steam; so retrofit of a thermal oxidizer with heat recovery to produce steam may not be economically feasible. For instance, at most existing plants the steam-generating facilities have already been provided. It may be possible to save some fuel by idling existing boilers. However, boilers are being used increasingly for disposal of wastes from processes, and boilers thus used could not be idled. Further, favorable economics from an energy consumption standpoint would depend on whether acetonitrile and/or hydrogen cyanide were sold and therefore not available as a fuel and whether deep welling is legally allowed.[5]

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7. H. M. Walker, Monsanto Co., EPA Questionnaire (Apr. 28, 1972).

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9. M. A. Pierle, Monsanto Chemical Intermediates Co., letter dated Mar. 16, 1979, to EPA with comments on draft Acrylonitrile report.

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11. K. E. Blower, Sohio, letter dated Feb. 16, 1979, to EPA with comments on draft Acrylonitrile report.

12. M. A. Pierle, Monsanto Chemical Intermediates Co., letter dated Aug. 10, 1979, to EPA with information on air emissions from acrylonitrile plants during startup periods.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 3

GLYCERIN AND ITS INTERMEDIATES
(ALLYL CHLORIDE, EPICHLOROHYDRIN, ACROLEIN, AND ALLYL ALCOHOL)

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Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

II. INDUSTRY DESCRIPTION

A. INTRODUCTION

The synthesis of glycerin from propylene was selected for consideration because early estimates for total emissions of volatile organic compounds (VOC) from production operations were relatively high.

Several chemical intermediates, co-products, and by-products or waste products are manufactured in the various process steps for the synthesis of glycerin from propylene.[1,2] These intermediates, co-products, and by-products are relatively volatile and can generate large amounts of emissions during their manufacture, handling, or consumption in subsequent processing operations (see physical property data, Appendix A).

The three major routes for the synthesis of glycerin from propylene are the chlorination route, in which the major intermediates are allyl chloride and epichlorohydrin; the oxidation route, in which the major intermediates and co-products are acrolein, allyl alcohol, and methyl ethyl ketone; the isomerization, peracetic acid route, in which propylene oxide is isomerized to allyl alcohol and then oxidized to glycidol and hydrolized to glycerin.[1,2] A variation of the propylene oxidation process in which excess air is present is used to produce acrolein and acrylic acid (see Sect. III.C.4).

Glycerin is a liquid with moderate viscosity and low vapor pressure (0.1 Pa) at ambient conditions. It is a relatively bland and innocuous material with a wide spectrum of uses, including humectants, emolients, ointments, and related internal and external applications.[1]

The major intermediates, co-products, and by-products generated in the synthesis of glycerin from propylene are liquids of low to moderate viscosity and moderate to high vapor pressure at ambient temperature. Most of these intermediates, co-products, and by-products are toxic and/or flammable materials; vapor release in significant quantities or concentrations could present serious problems (see Appendix A for typical physical properties).

B. USAGE AND GROWTH (DOMESTIC)[1,3,4]

Table II-1 shows production and growth rates for synthetic glycerin and the principal intermediates. Synthetic glycerin has a zero to slightly negative growth rate, since glycerin from natural sources is taking an ever larger share of the total glycerin market. Before 1974 synthetic glycerin had 57% of the glycerin market share, whereas natural glycerin's market share was 43%. After 1974 the increase in oil pricing caused the price of synthetic glycerin to rise sharply, and it is now about 4¢ higher than the price of natural glycerin. Because of this price differential market shares have changed, and synthetic glycerin now has only 49% of the total market and its market share is declining.

As a principal intermediate, acrolein is also used in the manufacture of other products, such as methionine. Approximately 60% of the total acrolein manufactured is subsequently converted to synthetic glycerin. Total acrolein usage is growing at about 2% per year.

The largest and most significant usage and growth pattern is exhibited by epichlorohydrin, an alternate intermediate for synthetic glycerin. Only about 25% of the total epichlorohydrin produced is converted to synthetic glycerin at present. The major use, approximately 56%, of epichlorohydrin is in the manufacture of epoxy resins. The overall growth rate in the use of epichlorohydrin is currently about 5.4% per year.

Propylene, the principal raw material for synthetic glycerin and its intermediates, is currently in ample supply and is expected to remain readily available. The past periodic shortages of chlorine, the other main raw material used in the chlorination process, will probably continue.

C. DOMESTIC PRODUCERS[1,3--7]

As of 1977 there were two domestic producers of acrolein, two domestic producers of epichlorohydrin, and three domestic producers of synthetic glycerin. Table II-2 lists the producers, the plant locations, the processes being used, and the nameplate capacity for the products being made. Figure II-1 shows the plant locations and products made at each location.

Table II-1. Production and Growth (Domestic) of Synthetic Glycerin and Major Intermediates*

	Synthetic Glycerin		Crude Epichlorohydrin		Acrolein	
Year	Production (Gg/yr)	Growth (%/yr)	Production (Gg/yr)	Growth (%/yr)	Production (Gg/yr)	Growth (%/yr)
1969	85.3		132		21.8	
1970	86.6	1.5	129	-2.3	21.8	
1971	87.0	0.6	129		21.8	
1972	90.3	3.8	138	7.0	21.3	-2.3
1973	94.3	4.4	155	12.3	24.9	16.9
1974	92.0	-2.5	166	7.1	24.0	-3.6
1975	61.7	-32.9	115	-30.7	18.6	-22.5
1976	70.7	16.2	144	25.2	20.4	9.7
1977	59.0	-17.7	132	-8.3	20.4	
		-4.5 Avg				-0.8 Avg
Est 1982	56.7	-0.8	172	5.4	22.7	2.0

*See refs 1, 3, and 4.

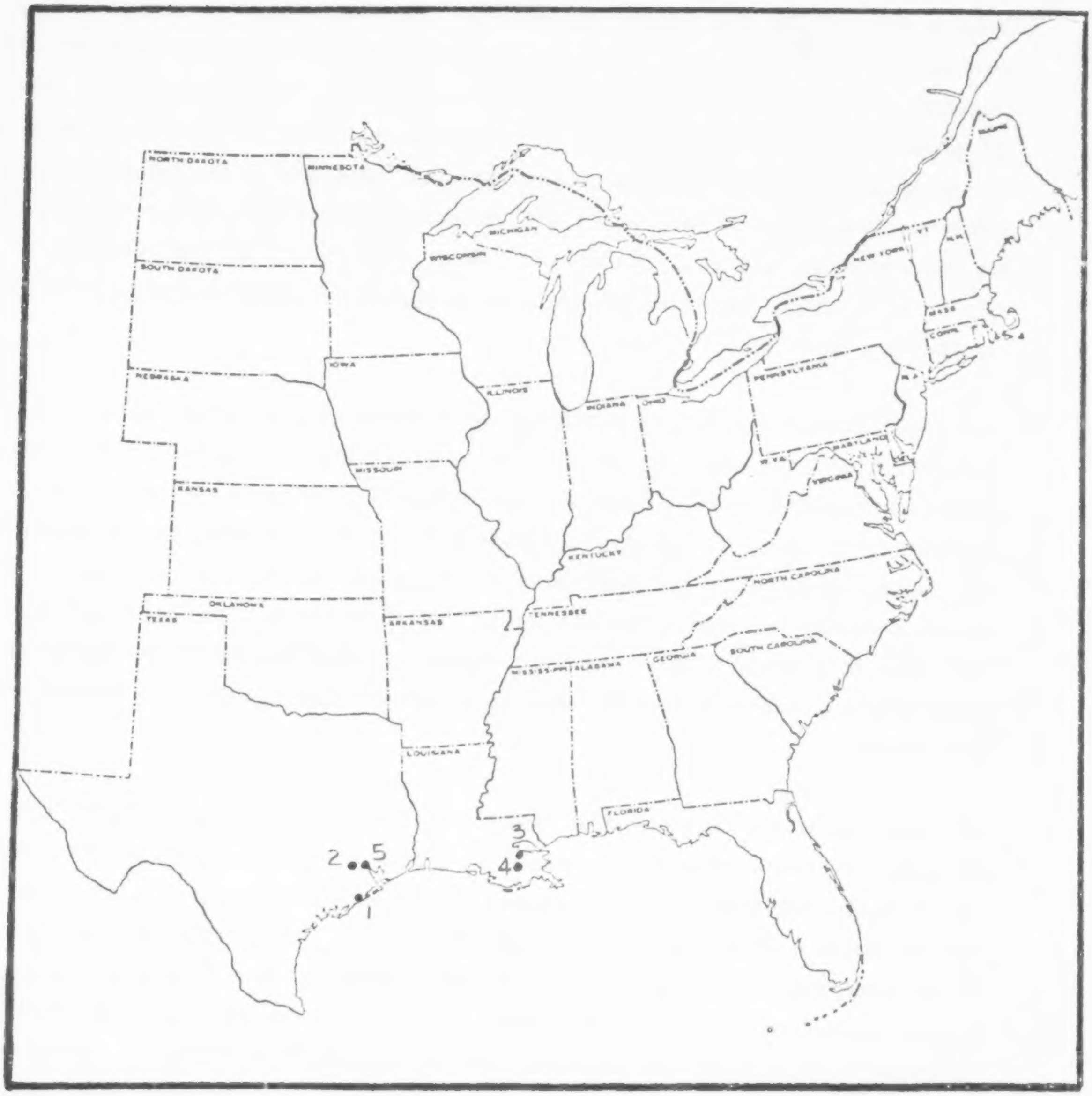
Table II-2. Capacity (Domestic) of Major Intermediates and Synthetic Glycerin[a]

Company	Location	Capacity (Gg/yr)			Process Type
		Acrolein	Crude Epichlorohydrin	Synthetic Glycerin	
Dow Chemical Co.	Freeport, TX		113.4	54.4	Chlorination
Shell Chemical Co.	Deer Park, TX		49.9		Chlorination
	Norco, LA		**49.9**	45.4[b]	Chlorination
	Norco, LA	24.9			Oxidation
Union Carbide Corp.	Taft, LA	27.2			Oxidation
FMC Corp.	Bayport, TX	——	——	18.1	Propylene oxide, peroxidation
Total		52.1	213.2	117.9	

---

[a] See refs 1, 3—7.

[b] Total combined synthetic glycerin capacity of Deer Park, TX, and Norco, LA, plants of Shell. Capacity breakdown for amounts of glycerin derived from epichlorohydrin vs acrolein is considered confidential by Shell.


NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
WISCONSIN
MICHIGAN
NEW YORK
VT
N.H.
MAINE
MASS
CONN
IOWA
NEBRASKA
ILLINOIS
INDIANA
OHIO
PENNSYLVANIA
N.J.
MISSOURI
W.VA.
MARYLAND
VIRGINIA
KANSAS
KENTUCKY
NORTH CAROLINA
OKLAHOMA
TEXAS
ARKANSAS
TENNESSEE
SOUTH CAROLINA
MISSISSIPPI
ALABAMA
GEORGIA
LOUISIANA
FLORIDA
1
2
3
4
5

1. The Dow Chemical Co., Freeport, TX, epichlorohydrin and glycerin.
2. Shell Chemical Co., Deer Park, TX, epichlorohydrin and glycerin.
3. Shell Chemical Co., Norco, LA, acrolein, epichlorohydrin, and glycerin.
4. Union Carbide Corp., Taft, LA, acrolein.
5. FMC Corp., Bayport, TX, glycerin.

Fig. II-1. Plant Locations and Products

Approximately 85% of the total synthetic glycerin capacity is based on the chlorination process and the oxidation process. The remaining 15% is based on a process in which propylene oxide is isomerized to allyl alcohol and the allyl alcohol is oxidized with peracetic acid to glycidol. The glycidol is then hydrolized to glycerin and purified. Sales of synthetic glycerin for 1977 were only 50% of nameplate capacity, and future markets are expected to shrink slightly from current levels. With this small and shrinking market for synthetic glycerin, no new synthetic glycerin plants are likely to be built in the near future, and one or more of the existing plants will probably discontinue the production of synthetic glycerin.

The capacity for acrolein manufacture is divided almost evenly between two manufacturers, but the end uses of the acrolein produced are aimed at radically different markets. Shell Chemical Co. converts a large share of its total acrolein production to synthetic glycerin, whereas Union Carbide does not manufacture any synthetic glycerin but aims most of its acrolein production toward conversion into methionine and miscellaneous uses. The production levels of acrolein for 1977 were only about 39% of nameplate capacity, and estimates of future growth rates (2%/yr) indicate that no additional production capacity is needed in the near future.

The capacity for epichlorohydrin manufacture is divided almost evenly between two manufacturers. The 1977 production levels of epichlorohydrin were about 62% of nameplate capacity, and production rates are estimated to increase at a rate of about 5.4% per year. At this growth rate, production should reach 90% of the nameplate capacity in 1984; so new production facilities will probably be constructed by or before that date. Most of the epichlorohydrin produced is consumed internally by the producers in the manufacture of such products as epoxy resins, elastomers, synthetic glycerin, and miscellaneous uses, with only a minor amount sold directly for use by others.

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7. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Shell Chemical Co. Process at Norco, LA, Jan. 25, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

III. PROCESS DESCRIPTIONS[1]*

A. INTRODUCTION

Three major processes are used to manufacture synthetic glycerin in the United States. Approximately 50% is made by the chlorination route from the intermediates allyl chloride and epichlorohydrin. Approximately 25% is made by the oxidation route from the intermediates acrolein and allyl alcohol. Approximately 25% is made from the intermediates propylene oxide and allyl alcohol. The projected growth rate for synthetic glycerin is minus 0.8% per year at present.[2]

Two of the processes are important because of the intermediates they produce. The chlorination route produces epichlorohydrin, which has become a major product as a precursor for epoxy resins and epichlorohydrin elastomers. Only about 25% of the total epichlorohydrin domestically manufactured is currently converted to synthetic glycerin, with the balance used for other purposes. The oxidation route produces acrolein, which has become another major product in its own right. About 60% of the total acrolein domestically manufactured is currently converted to synthetic glycerin, with the balance going for other uses.[2]

Propylene oxide is a major commodity chemical with varied uses. Only about 1.8% of the total propylene oxide domestically produced is currently consumed in the manufacture of synthetic glycerin by the isomerization-hydroperoxidation route.[2]

The major competitor for glycerin markets is "natural" glycerin from a large and varied list of suppliers. Natural glycerin is derived from triglycerides of various fatty acids found in nature. The raw materials include animal fats (tallow) and vegetable oils from various sources. About 25 different domestic companies produce crude natural glycerin as a by-product in their processing operations using natural fats and oils. About 12 of these domestic companies refine their crude natural glycerin to U.S.P. glycerin. Synthetic glycerin sells for about $0.63 per lb, and refined natural glycerin sells currently for about $0.54 per lb as of February 1980. Given this price differential, it is obvious why the natural glycerin is increasing its share (about 57%) of the total glycerin market, whereas the market share for synthetic glycerin is shrinking.[3] Because of the complexity of the processes involved and because of the need to ensure that process vent emissions are properly identified and quantified, process vents are grouped and discussed in separate sections labeled as "Main Process Vents" for each major process route. Process descriptions are somewhat generalized and do not necessarily exactly represent the processing schemes employed by individual producers.

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*Except where indicated by another reference number, the data in this section were taken from ref. 1 (see "References" at end of the section).

B. CHLORINATION PROCESS

1. Basic Reactions and Process Description

Synthetic glycerin is produced from propylene, chlorine, and alkali in a three-step series of reactions. Refer to Figs. III-1.A—C respectively for model-plant flowsheets for the intermediates allyl chloride, epichlorohydrin, and glycerin. In the first step (Fig. III-1.A) propylene is reacted adiabatically with chlorine in a high-temperature gas-phase reactor to produce allyl chloride. A simple illustration of this reaction is

$$CH_2{=}CH{-}CH_3 \ + \ Cl_2 \ \longrightarrow \ CH_2{=}CHCH_2Cl \ + \ HCl$$

This reaction is extremely rapid. The optimum peak reaction temperature is about 500°C. Excess propylene is used to dilute the reaction and to minimize side reactions. Peak reaction temperatures are controlled, and the reactor configuration is designed to maximize product yield and minimize side reactions. Some by-products that are generated in this reaction step are chloropropene, dichloropropene, and dichloropropane. Miscellaneous tars and carbonaceous by-products are also generated in this high-temperature reaction (see Reaction Section, Fig. III-1.A).

When the hot gas exits the reactor, it is immediately quench cooled by a cold stream of liquid propylene injected into the hot gas. Further cooling by propylene evaporation condenses the allyl chloride and other chlorinated organics in the reactor gas. This gas-liquid mixture is then fractionated to separate the HCl and propylene from the liquid products (see Initial Separation Section, Fig. III-1.A).

The propylene-HCl gas stream is then compressed, partly condensed, and fractionated to separate pure HCl gas from the propylene. The pure HCl gas either is put

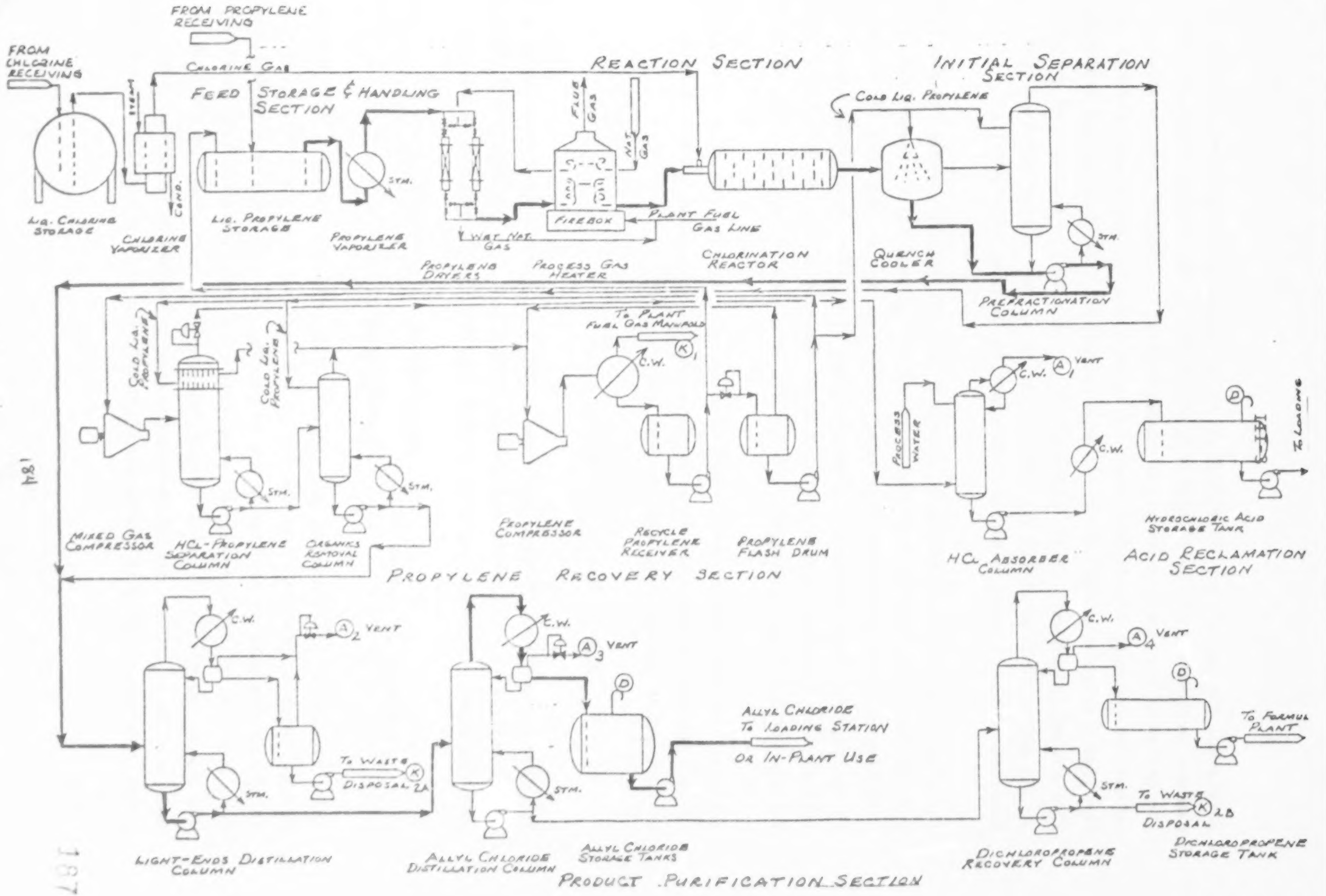

FROM CHLORINE RECEIVING
FROM PROPYLENE RECEIVING
CHLORINE GAS
STEAM
COND.
LIQ. CHLORINE STORAGE
CHLORINE VAPORIZER
FEED STORAGE & HANDLING SECTION
LIQ. PROPYLENE STORAGE
PROPYLENE VAPORIZER
STM.
PROPYLENE DRYERS
WET NAT. GAS
REACTION SECTION
FLUE GAS
NAT. GAS
FIREBOX
PLANT FUEL GAS LINE
PROCESS GAS HEATER
CHLORINATION REACTOR
INITIAL SEPARATION SECTION
COLD LIQ. PROPYLENE
QUENCH COOLER
PREFRACTIONATION COLUMN
COLD LIQ. PROPYLENE
COLD LIQ. PROPYLENE
TO PLANT FUEL GAS MANIFOLD
C.W.
K 1
MIXED GAS COMPRESSOR
HCL-PROPYLENE SEPARATION COLUMN
ORGANICS REMOVAL COLUMN
PROPYLENE COMPRESSOR
RECYCLE PROPYLENE RECEIVER
PROPYLENE FLASH DRUM
PROPYLENE RECOVERY SECTION
PROCESS WATER
A 1 VENT
HCL ABSORBER COLUMN
D
TO LOADING
HYDROCHLORIC ACID STORAGE TANK
ACID RECLAMATION SECTION
A 2 VENT
TO WASTE DISPOSAL
K 2A
A 3 VENT
ALLYL CHLORIDE TO LOADING STATION OR IN-PLANT USE
A 4 VENT
TO FORMUL PLANT
TO WASTE DISPOSAL
K 2B
LIGHT-ENDS DISTILLATION COLUMN
ALLYL CHLORIDE DISTILLATION COLUMN
ALLYL CHLORIDE STORAGE TANKS
DICHLOROPROPENE RECOVERY COLUMN
DICHLOROPROPENE STORAGE TANK
PRODUCT PURIFICATION SECTION

Fig. III-1.A. Uncontrolled Model-Plant Flowsheet for Production of Allyl Chloride

into a HCl gas header for use elsewhere in the plant or is absorbed in water to produce technical-grade hydrochloric acid for sale. The liquid propylene from the bottom of the gas fractionation column is sent to another fractionation column for recovery of residual higher boiling organics, which are returned to the liquid allyl chloride stream. The propylene gas from this second fractionation column is compressed and condensed for recycle to the process and for use as the quench cooling liquid for rapid chilling of the reactor effluent (see Propylene Recovery Section and Acid Reclamation Section, Fig. III-1.A).

The crude allyl chloride is fed to a series of distillation columns for purification of the allyl chloride and separation of the various waste streams and by-products Dichloropropene is a valuable by-product that is recovered and sold for use as an agricultural soil fumigant. A small amount of purified allyl chloride is sold or used for other products, but most of the allyl chloride is used as feedstock for the epichlorohydrin process (see Product Purification Section, Fig. III-1.A).

The next reaction step is the synthesis of epichlorohydrin from allyl chloride. In this process sequence chlorine gas is dissolved in a large excess of water to form acidic hypochlorous acid as follows:

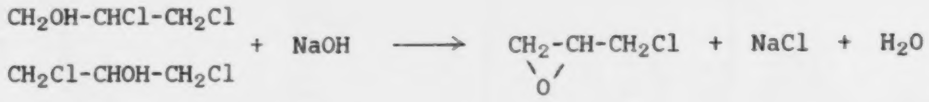
$$Cl_2 + H_2O \leftrightarrows HOCl + HCl$$

The allyl chloride is blended into this dilute hypochlorous acid solution at a low concentration (to prevent the formation of a separate oil layer) and reacts with the aqueous hypochlorous acid to form glycerin dichlorohydrin as follows:

$$CH_2{=}CH{-}CH_2Cl + HOCl \longrightarrow \begin{array}{l} CH_2Cl{-}CHOH{-}CH_2Cl \ (30{-}35\%) \\ CH_2OH{-}CHCl{-}CH_2Cl \ (65{-}70\%) \end{array}$$

This reaction is influenced by pH, concentration, and temperature. The pH must be kept below 6, preferably in the 0.4 to 1.0 region. The concentration of allyl chloride must be kept quite low to prevent the formation of a second phase (oil layer) since the presence of a separate oily phase promotes side reactions and lowers the yields of the desired dichlorohydrin. Reaction temperatures are moderate (40 to 50°C). An intense mixing zone is needed at the point where allyl chloride is added to the aqueous hypochlorous acid to rapidly and thoroughly disperse the allyl chloride in the aqueous phase. Some of the by-products or waste materials generated in this reaction step are trichloropropane, tetrachloropropyl ether, and various chlorinated aldehydes and ketones (see Reactor System, Fig. III-1.B).

When the hypochlorination reaction is complete, the dilute reaction solution is reacted with an alkali source (such as calcium carbonate) to neutralize the hydrochloric acid present and to convert the glycerin dichlorohydrin to epichlorohydrin as follows:



$$\begin{matrix} CH_2OH\text{-}CHCl\text{-}CH_2Cl \\ CH_2Cl\text{-}CHOH\text{-}CH_2Cl \end{matrix} + NaOH \longrightarrow \underset{\diagdown O \diagup}{CH_2\text{-}CH}\text{-}CH_2Cl + NaCl + H_2O$$

This reaction step is influenced by temperature and reactant concentration. The reaction mixture from the chlorohydrination step is normally quite dilute (3 to 5%) and the temperature is moderate (40 to 50°C). A slight excess (about 5%) of alkali is used to drive the epoxidation step to completion. Some of the by-products or waste materials generated in this reaction step are glycerin monochlorohydrin, glycidol, glycerin, and miscellaneous higher molecular weight materials such as polyglycols and chloroethers (see Epoxidation Reactor, Fig. III-1.B).

After the alkaline epoxidation step the epichlorohydrin is stripped from the reaction mixture by azeotropic distillation. Since epichlorohydrin azeotropically distills with water at 26% water and since the saturation level of water in epichlorohydrin is only about 2%, the condensate consists of two phases. The water layer containing dissolved epichlorohydrin is returned to the primary azeotrope still as reflux, and the epichlorohydrin layer containing dissolved water is fed as reflux to a secondary stripping column that azeotropically strips the dissolved water out of the epichlorohydrin product. The overhead condensate from the secondary stripping column also condenses as two phases; this condensate is also separated, with the water layer going back to the primary column while the organic layer goes to the top of the secondary column (see Azeotrope Column and Drying Column, Fig. III-1.B).

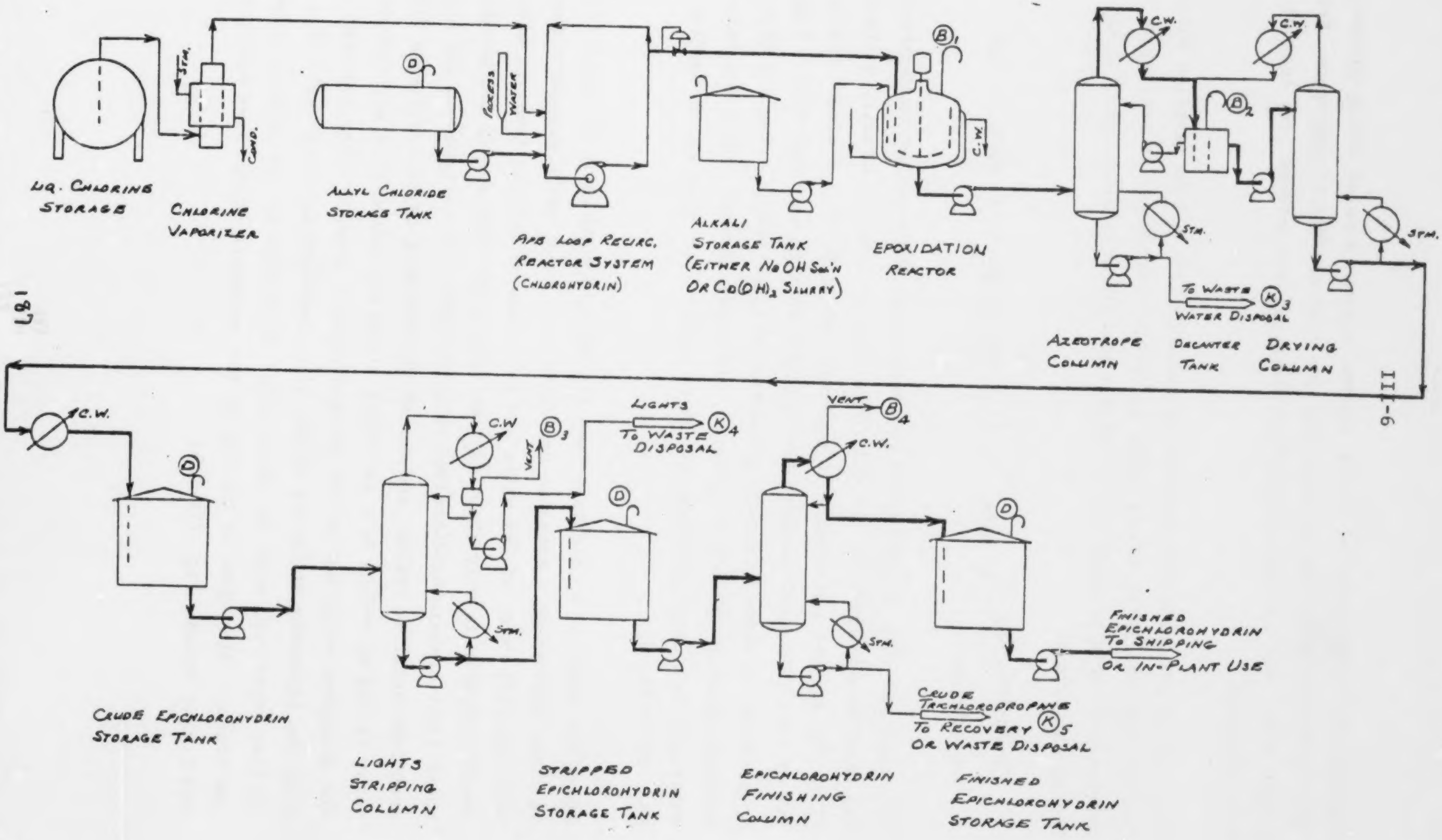
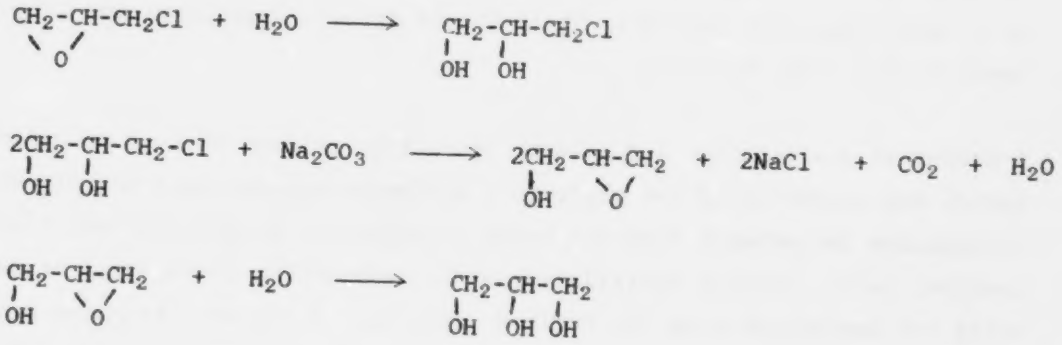

LIQ. CHLORINE STORAGE
STM.
COND.
CHLORINE VAPORIZER
D
ALLYL CHLORIDE STORAGE TANK
PROCESS WATER
APB LOOP RECIRC. REACTOR SYSTEM (CHLOROHYDRIN)
ALKALI STORAGE TANK (EITHER NaOH Sol'n OR Ca(OH)2 SLURRY)
B1
C.W.
EPOXIDATION REACTOR
C.W.
C.W.
B2
STM.
STM.
TO WASTE WATER DISPOSAL
K3
AZEOTROPE COLUMN
DECANTER TANK
DRYING COLUMN
C.W.
D
CRUDE EPICHLOROHYDRIN STORAGE TANK
C.W
B3
VENT
STM.
LIGHTS
TO WASTE DISPOSAL
K4
LIGHTS STRIPPING COLUMN
D
STRIPPED EPICHLOROHYDRIN STORAGE TANK
VENT
B4
C.W.
STM.
CRUDE TRICHLOROPROPANE
TO RECOVERY
K5
OR WASTE DISPOSAL
EPICHLOROHYDRIN FINISHING COLUMN
D
FINISHED EPICHLOROHYDRIN TO SHIPPING OR IN-PLANT USE
FINISHED EPICHLOROHYDRIN STORAGE TANK

Fig. III-1.B. Uncontrolled Model-Plant Flowsheet for Production of Epichlorohydrin

The bottom stream from the primary azeotrope column is a large wastewater stream containing dissolved salt and the water-soluble organic waste materials generated by the chlorohydrination and epoxidation reaction steps.

After azeotropic distillation, the crude epichlorohydrin stream is sent to two distillation columns for removal of lights and distillation of refined epichlorohydrin. The bottoms from the epichlorohydrin distillation column contain the residual trichloropropane and other high boilers. The refined epichlorohydrin is either sold or transferred to another process unit for conversion to finished products such as epoxy resin or epichlorohydrin elastomers (see Lights Stripping Column and Epichlorohydrin Finishing Column, Fig. III-1.B).

In the glycerin processing system the epichlorohydrin is blended with a large stream of a dilute aqueous solution of sodium carbonate. This aqueous stream is then heated and held at elevated temperature to hydrolyze the epichlorohydrin to glycerin in a series of reactions as follows:



These series of reactions are temperature-dependent and so they either can be conducted in large tanks held near the boiling point for several hours or can take place in a few minutes in a high-temperature, high-pressure reaction coil. A slight excess of sodium carbonate is used to assure complete conversion of the epichlorohydrin to glycerin. Concentration of glycerin in the reactor effluent is about 20 to 25%. Impurities or by-products produced in this reaction consist principally of higher molecular weight glycol ethers and polyglycols.

When reaction is complete, the excess carbonate is neutralized with a small amount of hydrochloric acid. The carbon dioxide generated by the reaction is captured and absorbed in a gas scrubbing column, with dilute sodium hydroxide used as the absorber fluid. The resultant aqueous sodium carbonate is then used as the reaction solution in the glycerin hydrolysis reaction (see Glycerin Reaction Section, Fig. III-1.C).

The raw glycerin solution from the hydrolysis step is dilute and contains a large concentration of salt (10 to 15%). This solution is concentrated in a double- (or triple-) effect calendria style of evaporator to distill off some of the water from the glycerin solution. As the water is evaporated, the salt crystallizes and comes out of solution. The resultant raw glycerin/water/salt slurry is centrifuged to remove the salt crystals. A water rinse in the centrifuge strips residual glycerin from the surface of the salt crystals. The washed salt crystals are discharged from the centrifuge and collected for either disposal or reuse in an electrolytic chlor-alkali facility. A final calendria style of evaporator concentrates the centrifuged glycerin solution from about 45% to about 85%, and the residual salt that crystallizes out in this final evaporation step is also removed by a centrifuge (see Calendria Style Double-Effect Evaporators and Calendria Style Concentrator, Fig. III-1.C).

A series of distillation and solvent extraction columns is used to refine and purify the concentrated raw glycerin. A flasher column takes the glycerin overhead to separate the product from the heavy polyglycols, polyethers, and traces of residual salt. Various distillation and/or extraction columns can be used to strip off impurities from the refined glycerin. A solvent stripping column is used to remove residual solvent from the solvent extracted glycerin. A final-product column uses superheated steam as a sweep gas to take the refined glycerin overhead for product purification. The pure refined glycerin is finally processed through an activated carbon bed to remove trace impurities and color bodies. The final U.S.P. glycerin from the carbon bed adsorption columns is stored for shipment to customers (see Fig. III-1.C, p. 2).

2. Main Process Vents

a. Allyl Chloride[4,5] -- The following four main process vents are shown in Fig. III-1.A:

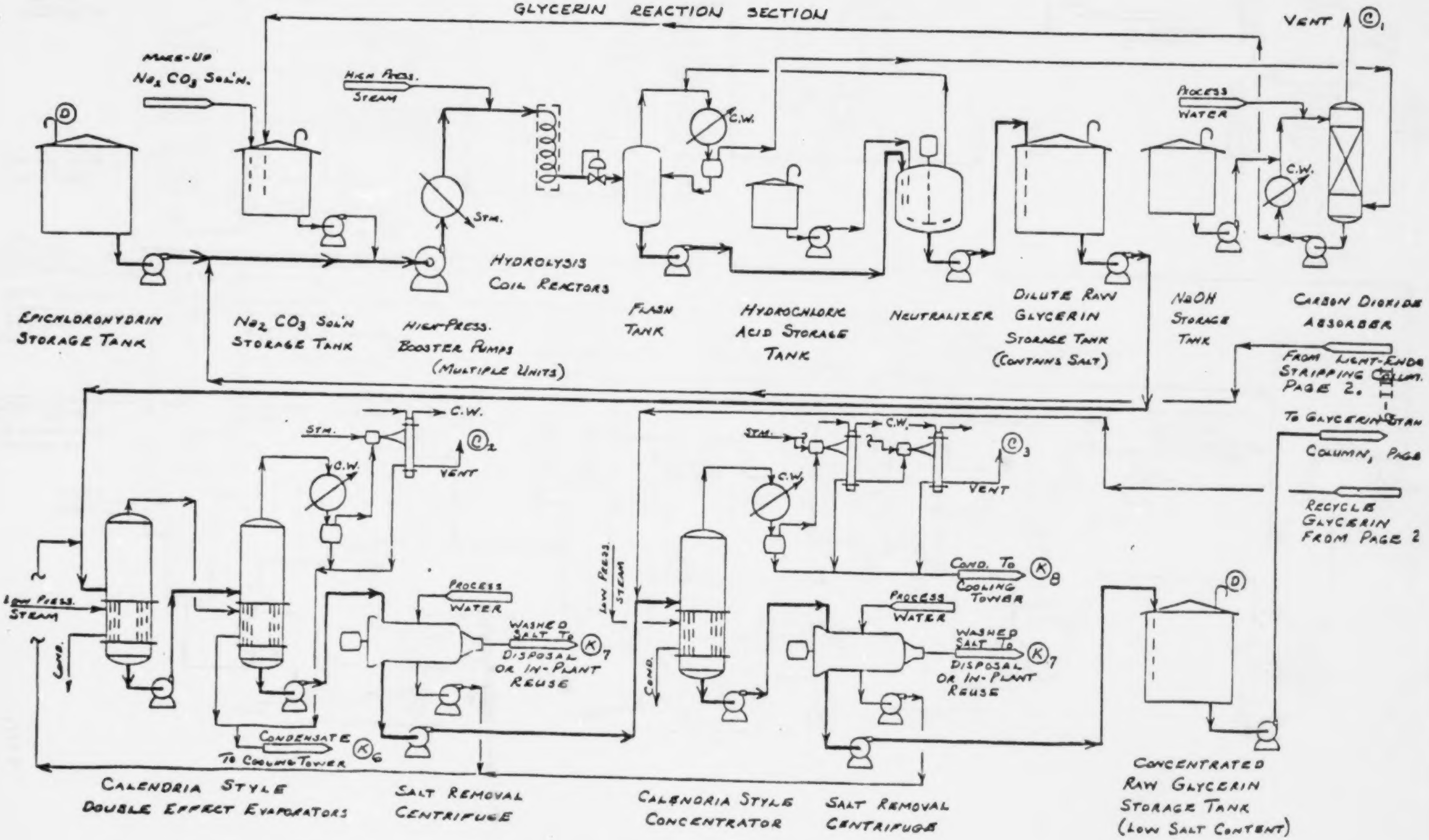

GLYCERIN REACTION SECTION
VENT
C1
MAKE-UP Na2 CO3 SOL'N.
HIGH PRESS. STEAM
C.W.
PROCESS WATER
C.W.
D
STM.
HYDROLYSIS COIL REACTORS
EPICHLOROHYDRIN STORAGE TANK
Na2 CO3 SOL'N STORAGE TANK
HIGH-PRESS. BOOSTER PUMPS (MULTIPLE UNITS)
FLASH TANK
HYDROCHLORIC ACID STORAGE TANK
NEUTRALIZER
DILUTE RAW GLYCERIN STORAGE TANK (CONTAINS SALT)
NaOH STORAGE TANK
CARBON DIOXIDE ABSORBER
FROM LIGHT-ENDS STRIPPING COLUM. PAGE 2.
TO GLYCERIN STRAN COLUMN, PAGE
RECYCLE GLYCERIN FROM PAGE 2
STM.
C.W.
C.W.
C2
VENT
STM.
C.W.
C.W.
C3
VENT
LOW PRESS. STEAM
LOW PRESS. STEAM
COND.
COND.
PROCESS WATER
WASHED SALT TO DISPOSAL OR IN-PLANT REUSE
K7
PROCESS WATER
WASHED SALT TO DISPOSAL OR IN-PLANT REUSE
K7
COND. TO COOLING TOWER
K8
CONDENSATE TO COOLING TOWER
K6
D
CALENDRIA STYLE DOUBLE EFFECT EVAPORATORS
SALT REMOVAL CENTRIFUGE
CALENDRIA STYLE CONCENTRATOR
SALT REMOVAL CENTRIFUGE
CONCENTRATED RAW GLYCERIN STORAGE TANK (LOW SALT CONTENT)

Fig. III-1.C. Uncontrolled Model-Plant Flowsheet for Production of Glycerin by the Chlorination Process

Page 1 of 2

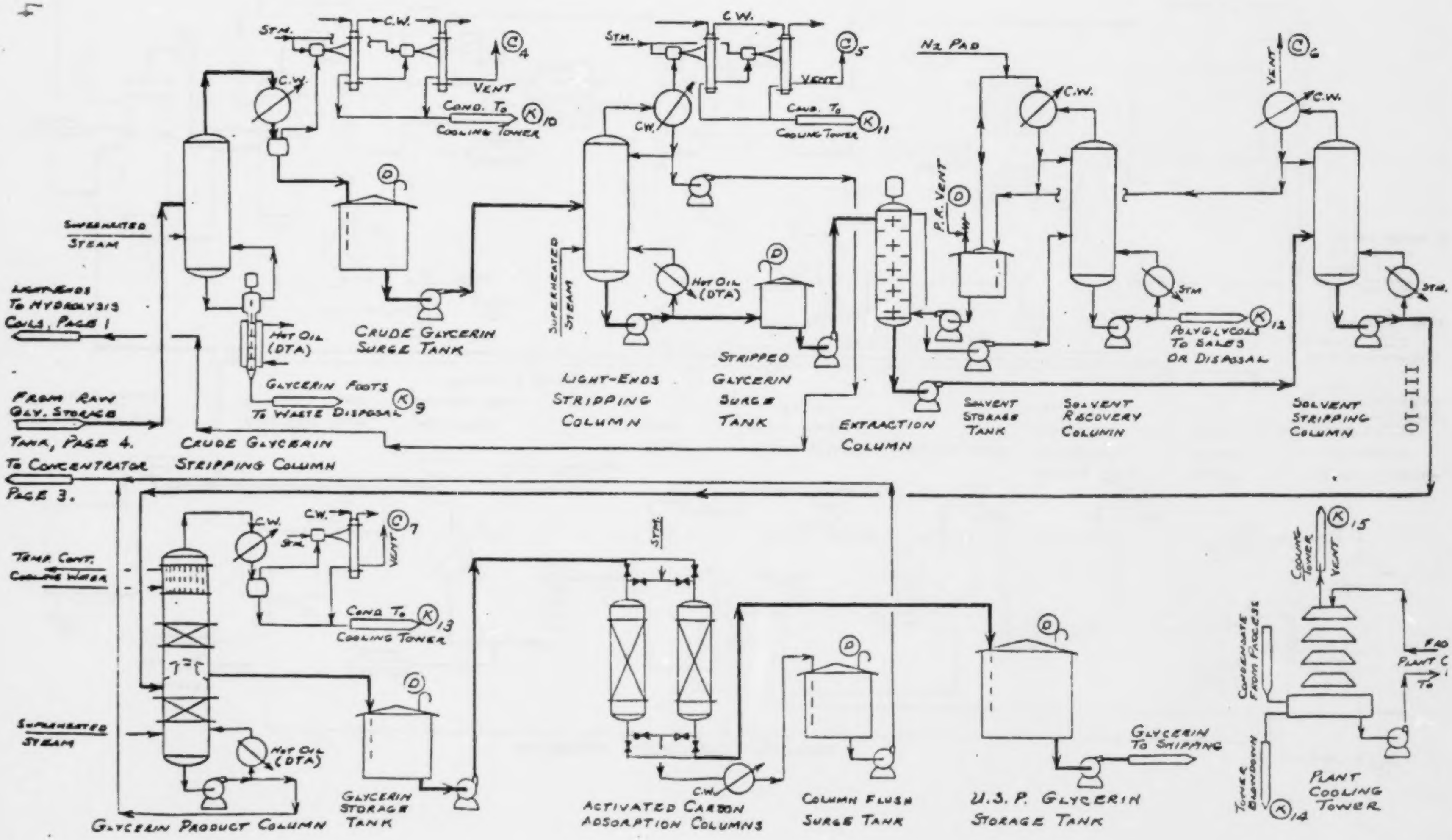

STM.
C.W.
C.W.
Ⓒ4
VENT
COND. TO COOLING TOWER
Ⓚ10
SUPERHEATED STEAM
LIGHT-ENDS TO HYDROLYSIS COILS, PAGE 1
HOT OIL (DTA)
Ⓓ
CRUDE GLYCERIN SURGE TANK
GLYCERIN FOOTS TO WASTE DISPOSAL
Ⓚ9
FROM RAW GLY. STORAGE TANK, PAGE 4.
TO CONCENTRATOR PAGE 3.
CRUDE GLYCERIN STRIPPING COLUMN
STM.
C.W.
Ⓒ5
VENT
COND. TO COOLING TOWER
Ⓚ11
C.W.
SUPERHEATED STEAM
HOT OIL (DTA)
Ⓓ
LIGHT-ENDS STRIPPING COLUMN
STRIPPED GLYCERIN SURGE TANK
EXTRACTION COLUMN
N2 PAD
P.R. VENT
Ⓓ
C.W.
SOLVENT STORAGE TANK
STM
POLYGLYCOLS TO SALES OR DISPOSAL
Ⓚ12
SOLVENT RECOVERY COLUMN
VENT
Ⓒ6
C.W.
STM.
SOLVENT STRIPPING COLUMN
C.W.
C.W.
STM.
Ⓒ7
VENT
COND TO COOLING TOWER
Ⓚ13
TEMP. CONT. COOLING WATER
SUPERHEATED STEAM
HOT OIL (DTA)
GLYCERIN PRODUCT COLUMN
Ⓓ
GLYCERIN STORAGE TANK
STM.
C.W.
ACTIVATED CARBON ADSORPTION COLUMNS
Ⓓ
COLUMN FLUSH SURGE TANK
Ⓓ
GLYCERIN TO SHIPPING
U.S.P. GLYCERIN STORAGE TANK
COOLING TOWER
VENT
Ⓚ15
CONDENSATE FROM PROCESS
TOWER BLOWDOWN
Ⓚ14
FRO PLANT C
TO
PLANT COOLING TOWER

Fig. III-1.C. (Continued)

Page 2 of 2

HCl absorber vent -- The HCl absorber vent located after the vent condenser discharges the inert gas from the chlorination process. This vent stream contains about 0.0001 to 0.0002 g of VOC per g of allyl chloride product. Principal components of the VOC in this vent stream are C_3 hydrocarbons such as propane and propylene (see Vent A_1, Fig. III-1.A).

Light-ends distillation column vent -- Low-boiling impurities are stripped out of the crude allyl chloride in this first distillation column. The vent stream contains about 0.05 to 0.08 g of VOC per g of allyl chloride product (see Vent A_2, Fig. III-1.A).

Allyl chloride distillation column vent -- This column distills the allyl chloride from the heavy impurities generated in the chlorination reaction. The vent stream can contain up to 0.0001 g of VOC per g of allyl chloride product. The principal component of the VOC in this vent stream is allyl chloride vapor (see Vent A_3, Fig. III-1.A).

Dichloropropene distillation column vent -- This column distills the dichloropropane-dichloropropene fraction from the rest of the "heavy" residues and tars. This vent stream can contain up to 0.001 g of VOC per g of allyl chloride product. The principal component of this VOC is dichlorinated C_3 hydrocarbon vapor (see Vent A_4, Fig. III-1.A).

b. Epichlorohydrin[4,5] -- The four main process vents shown in Fig. III-1.B are as follows:

Epoxidation reactor vent -- Dilute glycerol dichlorohydrin solution is reacted with an alkali source in this reaction vessel to convert the dichlorohydrin to epichlorohydrin. The vent gas from this reactor system contains chlorinated hydrocarbon vapors, such as epichlorohydrin and related materials. This vent stream can contain from 0.0002 to 0.02 g of VOC per g of epichlorohydrin product, depending on the reactor design, operating conditions, and type of alkali used (see Vent B_1, Fig. III-1.B).

Azeotrope column vent -- Crude epichlorohydrin is separated from the dilute salt solution in this distillation system. The vent gas from this column assembly contains some epichlorohydrin, as well as other low-boiling organic materials. This vent stream contains up to 0.0008 g of VOC per g of epichlorohydrin product (see Vent B_2, Fig. III-1.B).

Lights stripping column vent -- Low-boiling impurities are stripped out of the crude epichlorohydrin in the distillation column. The vent gas from this column contains some epichlorohydrin and lower boiling organic compounds, up to 0.008 g of VOC per g of epichlorohydrin product (see Vent B_3, Fig. III-1.B).

Epichlorohydrin finishing column vent -- Refined epichlorohydrin is produced by this distillation column. The principal organic material found in the vent gas from this column is epichlorohydrin, up to 0.0004 g of VOC per g of epichlorohydrin product (see Vent B_4, Fig. III-1.B).

It is possible to combine the three vent streams from these three separate distillation systems into one single vent by piping the column outlets into one common vent header.

c. Glycerin[5] -- Seven main process vents are shown in Fig. III-1.C as follows:

Carbon dioxide absorber vent -- Inert gas, water vapor, and traces of VOC are released from the vent after the carbon dioxide absorber. This vent gas contains about 0.0004 g of VOC per g of glycerin product (see Vent C_1, Fig. III-1.C, p. 1).

Double-effect evaporator vent -- This system concentrates the dilute, salty, glycerin stream to about 45% glycerin. The vent gas from the vacuum system on these evaporators is essentially inert gas and water vapor. It does not contain any significant amount of VOC (see Vent C_2, Fig. III-1.C, p. 1).

Calendrial style concentrator vent -- This system evaporates additional water from the crude glycerin stream, concentrating the crude glycerin from about 45% glycerin to about 85% glycerin. The vent gas from the vacuum system on this evaporator is essentially inert gas and water vapor. It does not contain any significant amount of VOC (see Vent C_3, Fig. III-1.C, p. 1).

Crude glycerin stripping column vent -- This system distills the crude glycerin overhead, leaving the polyglycols and other heavy materials in the bottoms from the distillation column. The vent gas from the vacuum system on this evaporator is essentially inert gas and water vapor. It does not contain any significant amount of VOC (see Vent C_4, Fig. III-1.C, p. 2).

Light-ends stripping column vent -- This system strips out the more volatile contaminates from the distilled crude glycerin. The vent gas from the vacuum system on this stripping column is essentially inert gas and water vapor. It does not contain any significant amount of VOC (see Vent C_5, Fig. III-1.C, p. 2).

Solvent stripping column vent -- After the solvent soluble contaminates are extracted from the distilled crude glycerin, the glycerin from the extraction system contains some dissolved solvent. This solvent is recovered by the solvent stripping column. The principal VOC contained in the vent gas from this column is the recovery solvent (acetone). This vent stream contains about 0.0002 g of VOC per g of glycerin product (see Vent C_6, Fig. III-1.C, p. 2).

Glycerin product column vent -- This column is used as the final-product distillation unit to produce pure glycerin. The vent from the vacuum system on this column is essentially inert gas and water vapor. It does not contain any significant amount of VOC (see Vent C_7, Fig. III-1.C, p. 2).

3. Fugitive and Secondary Emission Sources

Fugitive leaks throughout the process can be the source of various kinds of VOC emissions. Leaks can occur from valves, flanges, pumps, agitators, and compressors. Many of the chemicals handled in this series of processes are highly flammable and toxic; so the plant must be well maintained to minimize the exposure of operating personnel to dangerous concentrations of toxic fumes or vapors.[4,5]

In the Glycerin Section of the process, condensate from the evaporation of water during the concentration of glycerin is collected for reuse. Total condensate stream is about 5 g per g of glycerin product. Some of this condensate is used as makeup water for the cooling tower that provides cool water for the heat exchangers in the plant. This condensate contains significant amounts of dilute VOC (primarily acetone). This VOC in the tower cooling water is lost to the atmosphere. The amount of VOC emitted by this cooling tower operation is about 0.0028 g per g of glycerin product[5] (see Stream K_{15}, Fig. III-1.C, p. 2).

Waste streams from the various sections of the process can be a source of secondary emissions. The amount and type of emissions generated by these waste streams depend upon the handling systems and disposal techniques used on the waste streams. Waste streams and their normal disposal techniques for the various process sections are as follows:

a. Allyl Chloride[4,5]—— In the allyl chloride process three waste streams (labeled K) are shown on Fig. III-1.A as follows:

Propylene recovery system off-gas -- Some impure gas is released from the propylene recovery system. This off-gas contains propane and propylene, as well as some other volatile hydrocarbons. The prime method of disposal for this off-gas is to inject it into the plant fuel gas manifold so that it can be used as fuel in various plant gas-fired burners and furnaces. This gas burns cleanly and does not result in significant VOC emissions (see K_1, Fig. III-1.A).

Light-ends liquids -- The light ends that are stripped out of the crude allyl chloride consist principally of chlorinated C_3 compounds such as chloropropenes and isopropyl chloride. This material is usually sent to an incineration system for destruction. VOC emissions generated during handling and incineration are dependent on system design and oeprating conditions. This stream is fairly large (0.05 to 0.10 g per g of allyl chloride product); so the amount of VOC that could be emitted by poor handling practices or incomplete oxidation during incineration could be significant (see K_{2A}, Fig. III-1.A).

Heavy-ends liquids -- The heavy ends are the chlorinated residues and tars that remain after the by-product dichloropropene and dichloropropane are stripped out for sale as an agricultural fumigant. This heavy-ends liquid is collected and sent to an incinerator system for destruction (see K_{2B}, Fig. III-1.A).

b. Epichlorohydrin[4,5] -- In the epichlorohydrin process three waste streams (labeled K) are shown in Fig. III-1.B as follows:

Wastewater stream -- The wastewater stream is the bottoms from the epichlorohydrin azeotrope column after the epichlorohydrin is stripped out of the dilute aqueous reaction stream. This wastewater contains salt and traces of eipchlorohydrin, along with some water-soluble glycolic and chlorinated glycolic materials. This wastewater stream is extremely large (over 30 g of wastewater per g of epichlorohydrin product) and has less than 0.3% of organics, usually in the range of 0.05 to 0.1% (see K_3, Fig. III-1.B). The normal disposal technique is to send this wastewater to a biological oxidation treatment system.

Lights organic waste -- The overhead product from the lights stripping column consists primarily of low-boiling chlorinated C_3 compounds such as allyl chloride and related materials. This material is collected and sent to an incineration system for destruction. The stream may contain up to 0.004 g of VOC per g of epichlorohydrin product. The amount of VOC actually emitted to the air depends on the handling techniques used and the performance of the incinerator (see K_4, Fig. III-1.B).

Heavies organic waste -- The heavies from the epichlorohydrin finishing still consist primarily of trichloropropane, along with other high-boiling chlorinated C_3 compounds and miscellaneous tars. Since there is a limited market for trichloropropane, some of this material could be recovered and purified (distilled) for sale. It is also possible to recover some glycerin from the waste stream by water extraction and low-temperature hydrolysis. This waste stream is fairly large, containing up to 0.04 g of organic materials per g of epichlorohydrin product. The primary disposal technique for this waste stream is incineration. The amount of VOC actually emitted to the air depends on the handling techniques used and the performance of the incinerator (see K_5, Fig. III-1.B).

c. Glycerin[5] -- In the glycerin process there are four waste streams (labeled K) shown in Fig. III-1.C as follows:

Condensate -- Condensate is collected from the distillation of water in the glycerin evaporators and concentrator. This wastewater stream is discussed in Sect. III-B.3, paragraph 2.

Salt -- The washed salt from the salt centrifuges is collected and discharged as a waste stream from the glycerin finishing operation. The process yields about 0.7 g of salt per g of glycerin product. This waste stream of salt contains some water and traces of glycerin and could either be collected and recycled to an electrolytic chlor-alkali facility or be sent to the plant wastewater disposal facility (see K_7, Fig. III-1.C, p. 1).

Foots -- The bottoms or foots from the glycerin stripping column consist primarily of a complex mixture of polyglycerines, along with traces of water and some residual salt. SRI data[1] indicate that this stream contains about 0.06 g of polyglycerides per g of glycerin product. The waste stream is normally collected and sent to a plant incinerator for disposal (see K_9, Fig. III-1.C, p. 2).

Bottoms -- The bottoms from the solvent recovery column consist of a mixture of polyglycols and glycol ethers. This stream of polyglycols is collected and sold as a by-product (see K_{12}, Fig. III-1.C, p. 2).

C. OXIDATION PROCESS[6]

1. Basic Reactions and Process Description

Synthetic glycerin is produced from propylene and oxygen in a three-step series of reactions. Refer to Fig. III-2 for the model-plant block flowsheet. Other materials consumed in this series of reactions include sec-butanol, aluminum granules, hydrogen peroxide, and water.

In the first step propylene is reacted with oxygen in the presence of steam in high-temperature, gas-phase, catalytic tubular reactors to produce acrolein and by-product acetaldehyde. A simple illustration of this reaction is

$$CH_2{=}CH{-}CH_3 \quad + \quad O_2 \quad \longrightarrow \quad CH_2{=}CH{-}CHO \quad + \quad H_2O$$

This reaction is extremely rapid and exothermic. The reaction temperature is approximately 400°C, depending on the specific catalyst used to promote the selective oxidation of propylene to acrolein. Steam and/or excess propylene is used to control the process and minimize side reactions. The principal by-product generated by this reaction is acetaldehyde. Waste products include water, carbon

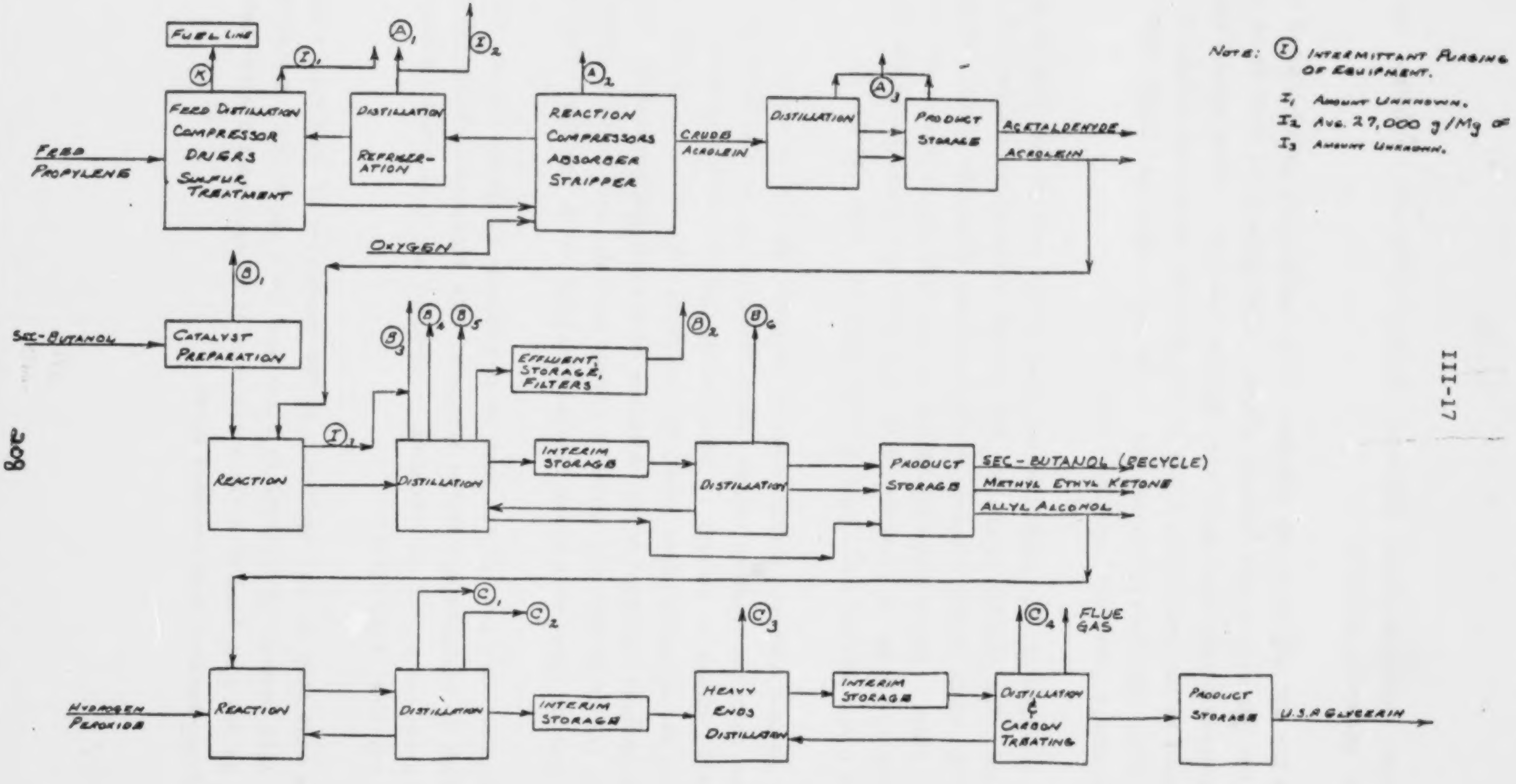

Feed Propylene
Fuel Line
K
Feed Distillation Compressor Driers Sulfur Treatment
I1
A1
I2
Distillation Refrigeration
A2
Reaction Compressors Absorber Stripper
Oxygen
Crude Acrolein
Distillation
A3
Product Storage
Acetaldehyde
Acrolein
Note: I Intermittant Purging of Equipment.
I1 Amount Unknown.
I2 Avg. 27,000 g/Mg of
I3 Amount Unknown.
B1
Sec-Butanol
Catalyst Preparation
Reaction
I1
B3
B4
B5
Distillation
Effluent, Storage, Filters
B2
Interim Storage
B6
Distillation
Product Storage
Sec-Butanol (Recycle)
Methyl Ethyl Ketone
Allyl Alcohol
Hydrogen Peroxide
Reaction
C1
C2
Distillation
Interim Storage
C3
Heavy Ends Distillation
Interim Storage
C4
Flue Gas
Distillation & Carbon Treating
Product Storage
U.S.P. Glycerin

Fig. III-2. Block Flowsheet of Oxidation Process for Uncontrolled Model Plant Producing Synthetic Glycerin

dioxide, carbon monoxide, and minor amounts of various aldehydes, ketones, and other oxidation products.

When the hot gas exits the reactor, it is immediately quench cooled by contacting the hot gas with a cool aqueous stream. Hydroquinone is used as an inhibitor to prevent polymerization of the reactive acrolein. After quench cooling, water is used as the absorption fluid in the carbonyl absorption column to strip acrolein and other oxygenated organics out of the gas stream (see block labeled Reaction, Compressors, Absorber, Stripper, Fig. III-2).

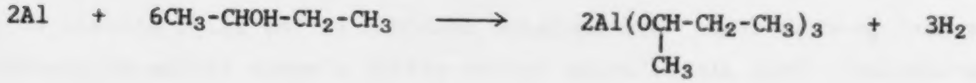
The stripped gas is compressed and then cooled in a carbon dioxide stripping column. The residual propylene and allied hydrocarbons are removed as a liquid, and the waste carbon dioxide (containing some flammable hydrocarbons) is vented to a flare. The liquid hydrocarbon stream from the bottom of the carbon dioxide stripping column is recycled to the propylene purification system for reuse (see block labeled Distillation, Refrigeration, Fig. III-2).

The aqueous acrolein stream from the carbonyl absorption system is fed to a crude acrolein recovery column, where the acrolein is distilled out of the water. A small stream of solvent is added to the top of the distillation column to break the acrolein-water azeotrope and permit dry acrolein to distill overhead. Hydroquinone is added to the acrolein to prevent polymerization. The bottoms from the crude acrolein recovery column separate into an oily organic layer and an aqueous layer (see block labeled Distillation on top line, Fig. III-2).

The crude, dry acrolein is sent to an aldehyde stripping column, where the acetaldehyde is stripped out of the acrolein. The finished acetaldehyde and the finished acrolein are stored for shipment or in-plant use (see block labeled Distillation on top line, Fig. III-2).

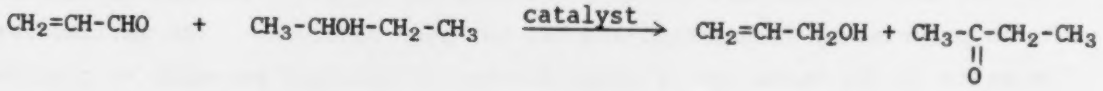
The next step in this synthesis is the conversion of acrolein to allyl alcohol. In this process sec-butanol is first sent to a sec-butanol drying column, where it is dry distilled with the assistance of an azeotrope-breaker solvent to separate the sec-butanol from residual water.

Some of the dry sec-butanol is reacted with aluminum granules to form aluminum butoxide (see block labeled Catalyst Preparation, Fig. III-2). The solution of aluminum butoxide in excess sec-butanol is used as a catalyst for the hydrogenation reaction. A simple equation for this catalyst forming reaction is



$$2Al + 6CH_3\text{-}CHOH\text{-}CH_2\text{-}CH_3 \longrightarrow 2Al(\underset{\substack{|\\ CH_3}}{OCH}\text{-}CH_2\text{-}CH_3)_3 + 3H_2$$

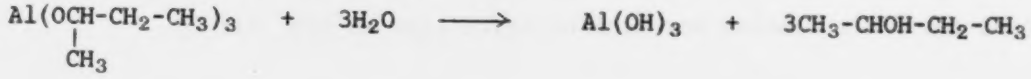
Acrolein is reacted with dry sec-butanol in the presence of aluminum butoxide catalyst to form allyl alcohol and methyl ethyl ketone. A simple equation for this hydrogenation reaction is



$$CH_2{=}CH\text{-}CHO + CH_3\text{-}CHOH\text{-}CH_2\text{-}CH_3 \xrightarrow{\text{catalyst}} CH_2{=}CH\text{-}CH_2OH + CH_3\text{-}\underset{\substack{\|\\ O}}{C}\text{-}CH_2\text{-}CH_3$$

The hydrogenation reaction is conducted in a liquid-phase hydrogenation reactor system at moderate temperature (about 50°C) for a moderate time (about 30 min) (see block labeled Reaction on second line, Fig. III-2).

Excess sec-butanol is used to drive the reaction to completion. After the hydrogenation reaction is completed, water is added to the reaction stream to kill the catalyst and precipitate the aluminum from the aluminum butoxide as aluminum hydroxide. A simple equation for this reaction is

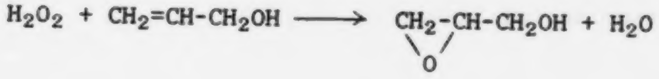


$$Al(\underset{\substack{|\\ CH_3}}{OCH}\text{-}CH_2\text{-}CH_3)_3 + 3H_2O \longrightarrow Al(OH)_3 + 3CH_3\text{-}CHOH\text{-}CH_2\text{-}CH_3$$

A filter system is then used to remove the precipitated aluminum hydroxide from the mixed reaction stream. This filter cake is contaminated with organics from the mixed reaction stream (see block labeled Effluent, Storage, Filters, Fig. III-2).

After filtration, the mixed reaction stream is sent to a series of distillation columns to separate the mixture into useful fractions. Residual acrolein, as well as traces of other low-boiling materials, are removed from the mixed reaction stream. These low boilers are recycled by adding them to the aqueous acrolein stream from the carbonyl absorption system. A solvent is added to the distillation column as an azeotrope breaker to assist in the dry distillation of methyl ethyl ketone and *sec*-butanol. Distilled methyl ethyl ketone is separated by this series of columns and is stored for sale as a by-product. Recovered *sec*-butanol is returned to the *sec*-butanol storage tank for recycle in the hydrogenation process. A concentrated solution of allyl alcohol in water is stored for use in the next process step. Hydroquinone is added to the allyl alcohol to inhibit polymerization. This distillation system yields a waste stream of heavies (see the two blocks labeled Distillation on second line, Fig. III-2).

The third synthesis step is the manufacture of glycerin from allyl alcohol by reaction with hydrogen peroxide and water. The catalyst system used to promote the initial reaction between allyl alcohol and hydrogen peroxide is considered to be proprietary information and has not been disclosed. The initial reaction sequence is the oxidation of allyl alcohol by hydrogen peroxide to glycidol, with the soluble catalyst acting as an intermediary in the reaction. The overall equation for this two-step oxidation is as follow:



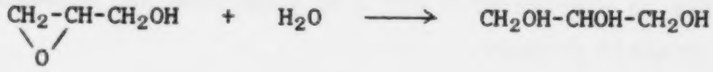
$$H_2O_2 + CH_2{=}CH{-}CH_2OH \longrightarrow \underbrace{CH_2{-}CH}_{O}{-}CH_2OH + H_2O$$

Conditions that favor this reaction and minimize side reactions are dilution with a large excess of water, reaction in the temperature range of 30 to 50°C, and control of the pH of the system within the range of 5 to 6. A slight excess of allyl alcohol is used to ensure complete consumption of the hydrogen peroxide (see the block labeled Reaction on third line of Fig. III-2).

After the oxidation step the soluble catalyst is extracted from the product stream and is recovered for recycle to the oxidation reactor system.

A light-ends stripper column is used to remove unreacted allyl alcohol and by-product acrolein from the aqueous oxidation product stream. The allyl alcohol is recycled for reuse in the process, and the low-boiling acrolein and associated impurities are collected for disposal (see the block labeled Distillation on the third line, Fig. III-2).

After the stripping process the glycidol-water solution is heated to accelerate the hydrolysis of glycidol to glycerin. Some conversion of glycidol to glycerin takes place in the oxidation reaction step, but additional exposure of glycidol to water at an elevated temperature is needed to complete the hydrolysis. The simple equation for this hydrolysis reaction is



$$\underset{\diagdown\,O\,\diagup}{CH_2\text{-}CH}\text{-}CH_2OH + H_2O \longrightarrow CH_2OH\text{-}CHOH\text{-}CH_2OH$$

The final reaction product is a dilute solution of glycerin. This solution also contains some higher boiling polyglycol heavy impurities and colored materials. A series of distillation columns are used to separate and purify the glycerin from this process (see the block labeled Heavy-Ends Distillation on line 3, Fig. III-2).

The distilled glycerin contains some residual colored impurities. This material is processed in a carbon bed adsorption system to remove the contaminates. The resultant U.S.P. glycerin is stored for sale. The residual material recovered by steam stripping of the carbon bed is recycled for recovery of the glycerin in the residue stream (see the block labeled Distillation and Carbon Treatment on line 3, Fig. III-).

2. Main Process Vents

a. Acrolein -- Acrolein is a volatile, highly toxic, highly irritating chemical with a very sharp, penetrating odor. Extreme care must be exercised in any process involving this material to prevent significant releases to the environment. This section has three process vents and one intermittent vent, indicated on Fig. III-2 as follows:

Carbon dioxide stripping tower vent -- This vent releases the carbon dioxide generated during the catalytic oxidation of propylene. The vent gas also contains some carbon monoxide, flammable hydrocarbon gases (such as propylene) and traces of oxidized hydrocarbons (such as acetaldehyde). This vent stream is normally vented to a flare to destroy the carbon monoxide and hydrocarbons.

This vent stream flow rate is about 0.61 g per g of acrolein product and it contains about 0.061 g of VOC per g of acrolein product (see A_1, Fig. III-2).

Refigeration vent, intermittent -- When the refrigerated condenser used to condense the propylene in the carbon dioxide stripping tower periodically plugs off due to frozen moisture, this vent is opened to defrost the condenser. This periodic venting releases an average of 0.027 g of propylene and associated C_3 hydrocarbons per g of acrolein product.

Aqueous acrolein system vent -- The carbonyl absorption column system discharges the crude aqueous acrolein to run tanks that are padded with methane. The absorber and the receiver are tied together and have a common vent. A vent scrubber is used to reduce the amount of acrolein vapor in the vent gas. The scrubber fluid is water, and the acrolein-containing scrubber fluid is returned to the process. After the methane vent gas is scrubbed, it still contains about 5% acrolein vapor and is sent to a flare to destroy the methane and acrolein vapor. The amount of vent gas from the scrubber to the flare is about 0.063 g per g of acrolein product and the crude acrolein contained in the gas is about 0.003 g per g of acrolein product (see A_2, Fig. III-2).

Distillation system vent -- The distillation system discharges refined acrolein to finished acrolein receiver tanks padded with methane. The column condenser and the receiver are tied together with a common vent line. The vent gas is sent to a flare to destroy the methane and acrolein vapor. The composition of the vent stream is about 95% methane and 5% acrolein. The flow rate of the vent stream going to the flare is about 0.15 g per g of acrolein product and it contains about 0.0075 g of acrolein per g of acrolein product (see A_3, Fig. III-2).

b. Allyl Alcohol -- Allyl alcohol is a toxic, irritating chemical with a very sharp, penetrating odor. Extreme care must be exercised in any process involving this material to prevent significant releases to the environment. There are six process vents in this section (see Fig. III-2) as follows:

Catalyst preparation vent -- When sec-butanol is reacted with aluminum granules in the preparation of aluminum butoxide catalyst, hydrogen is evolved and must be vented. This hydrogen vent gas contains some sec-butanol as VOC. The composition of the vent stream is about 65% hydrogen and 33% sec-butanol, with minor amounts of inert gases. This vent stream contains about 0.225 g of VOC per g of allyl alcohol product (see B, Fig. III-2).

Filtration system scrubber vent -- After reaction and water addition, the aluminum hydroxide precipitate is filtered out of the reactant stream. The filtration and cake handling system yields a vent stream that contains about 5% acrolein. The vent gas contains about 0.06 g of inert gas and 0.0032 g of VOC per g of allyl alcohol product (see B_2, Fig. III-2).

Lights stripper column vent -- After filtration, a lights stripper column is used to remove low boiling impurities from the product stream. This column and its associated receiver tank are padded with methane. The vent gas from this system contains about 50% methane, 25% acrolein, and 25% acetone and is sent to a flare to destroy the methane and other organics. The flow rate of this vent stream to the flare is about 0.023 g per g of allyl alcohol product, and the stream contains about 0.011 g of nonmethane VOC per g of allyl alcohol product (see B_3, Fig. III-2).

Distillation system condenser vents -- There are three separate distillation column condenser vents in the allyl alcohol distillation system. These distillation columns and their associated condenser vents have characteristic vent emissions of 0.00016 g, 0.0016 g, and 0.0095 g of VOC per g of allyl alcohol product respectively (see B_4, B_5, and B_6, Fig. III-2).

c. Glycerin -- There are four main process vents indicated on the Glycerin Section of Fig. III-2 as follows:

Light-ends stripper vent -- Residual low-boiling impurities, principally acrolein and allyl alcohol, are stripped out of the dilute aqueous reaction mixture. The vent gas from this stripper column is sent to a scrubber system for removal of these toxic vapors. The vent gas to the scrubber system contains about 14% VOC. This vent stream contains about 0.015 g of VOC per g of glycerin product (see C_1, Fig. III-2).

Concentrator column vent -- The dilute glycerin stream is concentrated by the water in the product being evaporated. The vent from this system contains very low levels of VOC, about 0.00015 g per g of glycerin product (see C_2, Fig. III-2).

Glycerin flasher column vent -- The crude, concentrated glycerin is flashed overhead in a vacuum stripping column to strip off the glycerin from the heavy polyglycol materials. The vent from the vacuum system for this column contains very low levels of glycerin as the primary VOC, about 0.00015 g per g of glycerin product (see C_3, Fig. III-2).

Product column vent -- A final-product distillation system is used to purify the raw glycerin after it is stripped from the heavy ends. Glycerin is distilled under vacuum to separate it out as a pure concentrated product. Bottoms from this column are recycled to the flasher column for recovery of residual glycerin. The vent from the vacuum system on this column contains very low levels of glycerin as the primary VOC, about 0.00015 g per g of glycerin product (see C_4, Fig. III-2).

3. Fugitive and Secondary Emission Sources

Leaks throughout the process can constitute sources of fugitive VOC emissions. They can occur from valves, flanges, pumps, agitators, and compressors. Many of the chemicals handled in this series of processes are highly flammable and toxic; therefore the plant must be well designed and maintained to minimize the exposure of operating personnel to dangerous concentrations of toxic fumes or vapors. It is common practice to use welded bonnets on valves and double mechanical seals with flush fluid on pumps, agitators, etc., to minimize fugitive leaks or losses of these toxic materials.

Waste streams from the various sections of the process can be a source of secondary emissions. The amounts and types of emissions generated by these waste streams depend on the handling systems and disposal techniques used. Information on the specific amounts and compositions of these waste streams is considered to be proprietary. Five types of secondary streams are generated by this series of processes as follows:

a. Fuel-Rich Waste Gas -- This type of waste stream is generated by the propylene purification and recovery systems associated with the acrolein step. The principal components are methane, ethane, ethylene, propane, and propylene. The principal technique for disposing of this material is to inject it into the plant fuel gas manifold for use as fuel (see K, Fig. III-2).

b. Liquid-Organic Streams -- Various liquid-organic secondary streams are generated in this process. Most of the streams contain various flammable and toxic chemicals. Typical sources would be the heavies and lights streams generated by the various distillation operations. The principal disposal technique is destruction by oxidation in a plant incinerator.

c. Aqueous Streams (Toxic) -- Wastewater streams containing dissolved toxic, volatile, or hazardous organics are generated at several process steps, including scrubbing of vent gases. Where possible, these aqueous streams are disposed of by reusing the contaminated water in the process. Those wastewater streams containing toxic organics that are not suitable for reuse in the process are injected into a deep-well disposal system.

d. Aqueous Streams (Nontoxic) -- Wastewater streams that do not contain significant quantities of toxic organics but still contain some dilute, relatively nonvolatile organic material are sent to the plant wastewater treatment system for bio-oxidation.

e. Contaminated Solid Wastes -- This process generates various solid wastes, such as filter cake, spent catalyst, and filter cartridges, that are contaminated with toxic and flammable chemicals. The principal technique for disposing of the contaminating organics is to burn the solids in a plant incinerator. For those solids not amenable to incineration, a chemical treatment is used to destroy the hazardous organic material before disposing of the solid wastes in a controlled landfill.

4. Process Variations

The main variations on the propylene oxidation process involve the conversion of propylene to acrolein. Variations in the catalyst used, in the reaction conditions, and in the reactor configuration can cause significant variations in product yields and amount and kind of by-products. The most significant variation is the use of air instead of purified oxygen as the source of oxygen for the propylene oxidation.

The use of air puts a large stream of nitrogen as an inert gas into the reactor system.

The nitrogen must be thoroughly scrubbed to remove acrolein and other reaction products from the gas stream before it is vented to the atmosphere. The ratio of propylene to oxygen is shifted to an oxygen-rich system to dodge the problem of recovering propylene from the vent gas. The use of excess oxygen changes the product yields and promotes the oxidation of acrolein to acrylic acid. The presence of significant quantities of acrylic acid in the aqueous acrolein product stream makes the recovery and purification of refined acrolein more difficult. Part or all of the combined gas-phase output stream from the oxidizer that converts propylene to acrolein oxidizer can be fed directly to another gas-phase oxidation reactor with a different catalyst to promote the conversion of acrolein to acrylic acid when the acrylic acid is the desired end product of the oxidation process.[7]

In the liquid-phase conversion of acrolein to allyl alcohol, other hydrogen donors can be used in place of sec-butanol; for example, ethanol, n-propanol, isopropanol, n-butanol, or isobutanol are all useful alcohols that can be converted to the equivalent aldehydes or ketones. None of these products are used commercially at present, however, since sec-butanol is a readily available refinery product and methyl ethyl ketone is a valuable by-product.

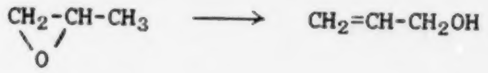
Acrolein can also be converted to allyl alcohol through vapor-phase hydrogen exchange with ethanol, but this process is not used commercially in the United States.

Allyl alcohol can be epoxidized to glycidol for conversion to glycerin by the use of peracetic acid instead of hydrogen peroxide. This particular process variation is practiced by the FMC Corporation in their synthesis of glycerin from propylene oxide.

D. ISOMERIZATION PROCESS

1. Basic Reactions and Process Description

The raw material for this process is propylene oxide. In the first step propylene oxide is isomerized to allyl alcohol in the presence of a slurry of a proprietary catalyst suspended in a high-boiling solvent. A simple equation for this process is

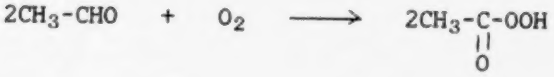


$$\underbrace{CH_2\text{-}CH}_{O}\text{-}CH_3 \longrightarrow CH_2{=}CH\text{-}CH_2OH$$

The reaction takes place at high temperature (about 300°C) and elevated pressures. Typical by-products of this reaction include propionaldehyde, acetone, n-propanol, acrolein, and a complex mixture of high-boiling tars.

The main-product stream exits from the isomerization reactor as a vapor and contains unreacted propylene oxide, allyl alcohol, and the low-boiling impurities. A series of condensation and distillation operations separate this product stream into propylene oxide for recycle, a lights waste stream, and an allyl alcohol product. Tars accumulate in the catalyst slurry and must be removed to prevent deactivation of the catalyst. A sidestream of catalyst slurry is removed from the isomerization reactor for treatment to remove the tars. The catalyst slurry is then recycled to the isomerization reactor. The tars emerge as a separate waste stream from the catalyst treatment system.

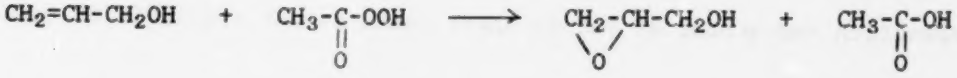
Peracetic acid is used as the source of oxygen in the epoxidation of allyl alcohol to glycidol. Peracetic acid is prepared by a controlled catalytic, liquid-phase oxidation of acetaldehyde with oxygen.[8] A simple equation for this reaction is



$$2CH_3\text{-}CHO \quad + \quad O_2 \longrightarrow 2CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}OOH$$

Acetic acid is a by-product in this controlled oxidation process. Separation and purification of the reaction products yield a peracetic acid stream suitable for use in various epoxidation reactions.

The epoxidation of allyl alcohol to glycidol by reaction with peracetic acid takes place according to the following simplified equation:

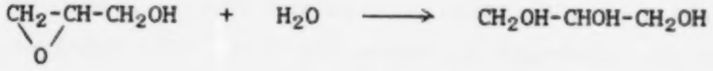


$$CH_2{=}CH\text{-}CH_2OH \quad + \quad CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}OOH \longrightarrow \underbrace{CH_2\text{-}CH}_{O}\text{-}CH_2OH \quad + \quad CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH$$

Low temperatures, short residence times, and the presence of an auxiliary solvent tend to minimize the formation of by-products. Typical by-products from this process are acetaldehyde, propionaldehyde, methyl acetate, acrolein, methanol, diallyl ether, allyl acetate, and n-propanol.

After reaction, distillation columns are used to separate the reaction products into useful components and waste streams. Excess allyl alcohol is recovered and recycled to the epoxidation reactor. Acetic acid is recovered, purified, and sold as a by-product. Waste streams of lights and heavies are collected for disposal. The inert solvent is recovered and recycled to the epoxidation reactor. The glycidol is collected and fed to the hydrolysis reactor.

Glycidol is hydrolyzed with excess water to convert it to glycerin. The simple reaction for this step is



$$\underset{\diagdown\ O\ \diagup}{CH_2-CH}-CH_2OH + H_2O \longrightarrow CH_2OH-CHOH-CH_2OH$$

A high temperature and excess water are used to promote this reaction. The by-products of the reaction are polyglycols and glycol ethers. After hydrolysis a series of distillation columns and auxiliary equipment are used to concentrate and purify the glycerin product. A waste stream of lights in water and a heavy waste stream are generated by this refining operation.

2. Main Process Vents

a. Isomerization -- The vents used in the isomerization process are those from the various distillation columns used to purify the product and recover the solvent from the catalyst regeneration operation. Information on the composition and amount of VOC in these vents is not available at this time.

b. Epoxidation Using Peracetic Acid -- The vents used in the peracetic acid epoxidation process are those from the various distillation columns used to purify the glycidol product and to recover the solvent used in the epoxidation process. Information on the composition and amount of VOC in these vents is not available at this time.

c. Glycerin -- The vents used in the glycerin process using glycidol from the peracetic acid epoxidation route are the same as those used in the glycerin process discussed previously in which glycidol is derived from hydroperoxide epoxidized allyl alcohol. For a detailed discussion of these vents, refer to Sect. III-C-2-c of this report.

3. Fugitive and Secondary Emission Sources

Leaks throughout the process can be sources of fugitive VOC emissions. Fugitive emissions can occur from valves, flanges, and moving shafts. Many of the chemicals are highly flammable and/or toxic; so the plant must be well designed and maintained to minimize the exposure of operating personnel to dangerous concentrations of toxic fumes or vapors.

Waste streams from the various sections of the process can be a source of secondary emissions. The amounts and types of emissions generated by these waste streams depend on the handling systems and disposal techniques used. Specific data on the amount and composition of these waste streams are not available at this time.

4. Process Variations

In the isomerization process for converson of propylene oxide to allyl alcohol the specific catalyst used affects the conversion rate and the ratio of allyl alcohol to the by-products. Vapor-phase isomerization techniques have been investigated and patented, but the only commercial operation in the United States is the liquid-phase isomerization process operated by the FMC Corporation at Bayport, TX.

Once allyl alcohol is produced by isomerization of propylene oxide, the rest of the process is similar to the Shell process for conversion of allyl alcohol to glycerin. FMC uses peracetic acid to epoxidize allyl alcohol to glycidol instead of using hydrogen peroxide and catalyst as Shell does. The use of peracetic acid involves the recovery of acetic acid from the glycidol product stream.

E. REFERENCES*

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2. S. L. Soder and K. L. Ring, "Propylene," pp. 300.5405E—300.5405L and 300.5405Q—300.5405R in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (August 1978).

3. D. Osterhof, "Glycerin," pp. 662.5021A—662.5023E in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1976).

4. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Shell Chemical Co. Process at Deer Park, TX, Jan. 25, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

5. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Dow Chemical Co. Process at Freeport, TX, Jan. 26 and 27, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

6. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Shell Chemical Co. Process at Norco, LA, Jan. 25, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

7. F. D. Bess, Union Carbide Corp., Taft, LA, letter to EPA, Apr. 21, 1978, in response to EPA request for information on the Union Carbide acrolein process.

8. H. J. Hagemeyer, "Acetaldehyde," pp. 100 and 109 in Kirk-Othmer Encyclopedia of Chemical Technology, 3d ed., Vol. 1, edited by M. Grayson et al., Wiley-Interscience, New York, 1978.

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. CHLORINATION PROCESS

1. Model Plant

The model-plant flowsheets (Figs. III-1.A—1.C) used for this study are not identical to either one of the existing commercial chlorination processes for the production of allyl chloride, epichlorohydrin, and glycerin, but they are close enough so that a study of their processes and emission points will give a valid understanding of the commercial operations.[1,2]

No estimates of typical raw-material, by-product, intermediates, or finished-product storage tank requirements have been made for this study.

2. Sources and Emissions

Emission factors and sources for the vents used in the chlorination process are summarized in Table IV-1.[2,3] The emission factors were derived from existing plant data, as well as from theoretical calculations in which vapor pressure and quantity of inert or sweep gas were used. No attempts have been made to estimate storage and handling, fugitive, or secondary emissions. The one known fugitive emission is included in the table.

B. OXIDATION PROCESS

1. Model Plant

The model-plant block flowsheet (Fig. III-2) used for this study is a copy of the block flowsheet furnished by Shell on their acrolein-glycerin process.[4]

Table IV-1. Uncontrolled VOC Emissions for the Chlorination Process Model Plant[a]

Process Step	Source	Stream Designation (Figs.III-1.A—C)	Emission Ratio (g/Mg)[b]	Principal Components of VOC Emission Streams[c]
Allyl chloride (Fig.III-1.A)				
	HCl absorber vent	A_1	100--200	C_3 hydrocarbons
	Light-ends dist. column vent	A_2	50,000--80,000	C_3 chlorinated hydrocarbons
	Allyl chloride dist. column vent	A_3	Up to 100	Allyl chloride
	Dichloropropene dist. column vent	A_4	Up to 1000	Dichlorinated C_3 hydrocarbons
Epichlorohydrin (Fig.III-1.B)				
	Epoxidation reactor vent	B_1	Up to 20,000	Epichlorohydrin
	Azeotrope column vent	B_2	Up to 800	Epichlorohydrin
	Lights stripping column vent	B_3	Up to 8000	C_3 chlorinated hydrocarbons
	Finishing column vent	B_4	Up to 400	Epichlorohydrin
Glycerin (Fig.III-1.C, pp. 1,2)				
	Carbon dioxide absorber vent	C_1	400	C_3 chlorinated hydrocarbons
	Evaporator vent	C_2	Less than 100	C_3 oxygenated hydrocarbons
	Concentrator vent	C_3	Less than 100	C_3 oxygenated hydrocarbons
	Stripping column vent	C_4	Less than 100	Glycerin
	Light-ends column vent	C_5	Less than 100	C_3 oxygenated hydrocarbons
	Solvent stripping column vent	C_6	200	Acetone
	Product column vent	C_7	Less than 100	Acetone
	Cooling tower	K_{15}	2800	Acetone

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[a] Refer to refs 2 and 3.

[b] g of total VOC per Mg of product produced.

[c] Only those components on which data were available are listed.

No estimates of typical raw material, by-product, intermediates, or finished-product storage tank requirements have been made for this study.

2. Sources and Emissions

Emission factors and sources for the vents from the oxidation process are summarized in Table IV-2.[4] No attempts have been made to estimate storage and handling, fugitive, or secondary emissions.

3. Process Variation

Process vent information has been furnished by Union Carbide on their variation of the oxidation process for the production of acrolein. They do not convert acrolein to allyl alcohol or allyl alcohol to glycerin. See Sect. III-C.4, paragraphs 1 and 2, for a description of this process variation. Their emission data on acrolein process vents is presented in Table IV-3. No attempts have been made to estimate storage and handling, fugitive, or secondary emissions.[5]

C. ISOMERIZATION PROCESS[1]

No attempt has been made to prepare model plant flowsheets or to estimate vent emissions from this process. The isomerization step in which propylene oxide is converted to allyl alcohol would have its own characteristic emissions. The peracetic acid manufacturing process in which acetaldehyde is oxidized to peracetic acid would also have its own characteristic emissions.[6] The conversion of allyl alcohol to glycidol and the hydrolysis of glycidol to glycerin would be somewhat different with peracetic acid used as the epoxidizing agent instead of hydrogen peroxide, but the characteristic emissions are expected to be similar to the emissions found for the glycerin sequence of the oxidation process shown in Table IV-2.

Table IV-2. Uncontrolled VOC Emissions for the Oxidation Process Model Plant[a]

Process Step	Source	Stream Designation (Fig.III-2)	Emission Ratio (g/Mg)[b]	Principal Components of VOC Emission Streams[c]
Acrolein				
	Carbon dioxide stripping tower vent	A_1	61,000	C_3 hydrocarbons (and carbon monoxide)
	Aqueous acrolein receiver vent	A_2	3,000	Acrolein (5%; methane, 95%)
	Distillation system vent	A_3	7,500	Acrolein (5%; methane, 95%)
	Refrigeration vent, intermittent	I_2	27,000	C_3 hydrocarbons (and carbon monoxide)
Allyl alcohol				
	Catalyst preparation vent	B_1	225,000	*sec*-Butanol (33%; hydrogen, 65%)
	Filtration system vent	B_2	3,200	Acrolein (5%; inert gas)
	Lights stripper column vent	B_3	11,000	Acrolein (25%), acetone (25%) (methane, 50%)
	Distillation system condenser vents	B_4	160	*sec*-Butanol and methyl ethyl ketone
		B_5	1,600	Allyl alcohol
		B_6	9,500	Methyl ethyl ketone
Glycerin				
	Light-ends stripper vent	C_1	15,000	Acrolein and allyl alcohol
	Concentrator column vent	C_2	150	C_3 oxygenated hydrocarbons
	Glycerin flasher column vent	C_3	150	Glycerin
	Product column vent	C_4	150	Glycerin

[a] Refer to ref 4.

[b] g of total VOC emission per Mg of product produced. VOC emissions exclude methane, carbon monoxide, and hydrogen, but include higher molecular weight organic compounds.

[c] Only those components on which data were available are listed.

Table IV-3. Uncontrolled VOC Emissions for the Union Carbide Variation of the Oxidation Process (Acrolein Only)[a]

Source	Stream Designation	Emission Ratio (g/Mg)[b]	Principal Components of VOC Emissions
Acrolein absorber vent	1	126,000	Acrolein, 0.61%, propane, 0.40%, and propylene, 0.61%
Combined distillation system vent header	2a-e	38,300	Acrolein, 77.7%, and acetaldehyde, 18.9%

[a] See ref 5.

[b] g of total VOC emission per Mg of acrolein produced.

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D. REFERENCES*

1. R. G. Muller, Glycerin and Intermediates, Report No. 58, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (December 1969).
2. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Dow Chemical Co. Process at Freeport, TX, Jan. 26 and 27, 1978 (on file at EPA, ESED, Research Triangle Park, NC).
3. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Shell Chemical Co. Process at Deer Park, TX, Jan. 25, 1978 (on file at EPA, ESED, Research Triangle Park, NC).
4. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Shell Chemical Co. Process at Norco, LA, Jan. 25, 1978 (on file at EPA, ESED, Research Triangle Park, NC).
5. F. D. Best, Union Carbide Corp., Taft, LA, letter to EPA, Apr. 21, 1978, in response to EPA request for information on the Union Carbide acrolein process.
6. H. J. Hagemeyer, "Acetaldehyde", pp. 100, 109 in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol 1, edited by M. Grayson *et al.*, Wiley-Interscience, New York, 1978.

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

V. APPLICABLE CONTROL SYSTEMS

A. CHLORINATION PROCESS[1—3]

A summary of controlled emissions for the chlorination process is given in Table V-1.

1. Allyl Chloride

a. HCl Absorber Vent (See Vent A, Fig. V-1.A)*——The stream from this vent contains residual propylene from the propylene-HCl stripping column. Proper design and operation of the stripping column is the key to maintaining low levels of propylene in the vent from the HCl absorber. It would be possible to collect this vent gas and send it to a plant flare for destruction, but the amount of VOC normally emitted is probably too low to justify the collection system piping that would be required. For a 113-Gg/yr plant the hourly emissions from this source would be about 1 to 3 kg.

b. Light-Ends Distillation Column Vent (See Vent A_2, Fig. V-1.A)——The stream from this vent is the largest single vent stream in the allyl chloride section of the process. For a 113-Gg/yr plant the hourly emissions from this source would be about 650 to 900 kg. The VOCs in the stream are low-value C_2-C_3 organics and chlorinated C_2-C_3 organics. Three possible options could be used to reduce these emission levels: (1) Installation of a refrigerated vent condenser to condense a large share of the VOC and return it to the condensate stream from this column. Depending on location, design, and operating conditions a vent condenser might remove 60 to 95% of the VOC.[4] (2) Collection of the vent stream and sending it to the plant flare system. A properly designed and operated flare system should destroy at least 98% of the VOC contained in the vent stream, but would cause the emission of HCl vapors to the atmosphere.[5] (3) Installation of an activated-carbon adsorption system to strip the VOC from the vent gas and collect the recovered VOC. A properly designed and operated adsorption system can remove at least 99% of the VOC. Vent gas incineration (flare) is probably the most cost-effective technique for removal of this VOC if HCl vapor emission can be tolerated. (A confined incinerator with water scrubbing could remove HCl from the flue gas.)

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*Figures V-1.A, B, and C and V-2 are duplicates of the flowsheets discussed in Sect. III.

Table V-1. Controlled VOC Emissions for the Chlorination Process Model Plant

Process Step	Source	Stream Designation (Fig.III-1)	Control Technique	Emission Reduction (%)	Emission Ratio* (g/Mg)
Allyl chloride					
	HCl absorber vent	A_1	None	0	100--200
	Light-ends dist. column vent	A_2	Flare	98	1,000--1,400
	Allyl chloride dist. column vent	A_3	None	0	Up to 100
	Dichloropropene dist. column vent	A_4	Scrubber	50	Up to 500
Epichlorohydrin					
	Epoxidation reactor vent	B_1	Use of NaOH or $Ca(OH)_2$	99	200
	Azeotrope column vent	B_2	Scrubber	84	130
	Lights stripping column vent	B_3	Flare	98	Up to 160
	Finishing column vent	B_4	None	0	Up to 400
Glycerin					
	Carbon dioxide absorber vent	C_1	None	0	400
	Evaporator vent	C_2	None	0	Less than 100
	Concentrator vent	C_3	None	0	Less than 100
	Stripping column vent	C_4	None	0	Less than 100
	Light-ends column vent	C_5	None	0	Less than 100
	Solvent strippping column vent	C_6	None	0	200
	Product column vent	C_7	None	0	Less than 100
	Cooling tower	K_{15}	Steam strip wastewater	95	140

*g of total VOC emissions per Mg of product produced.

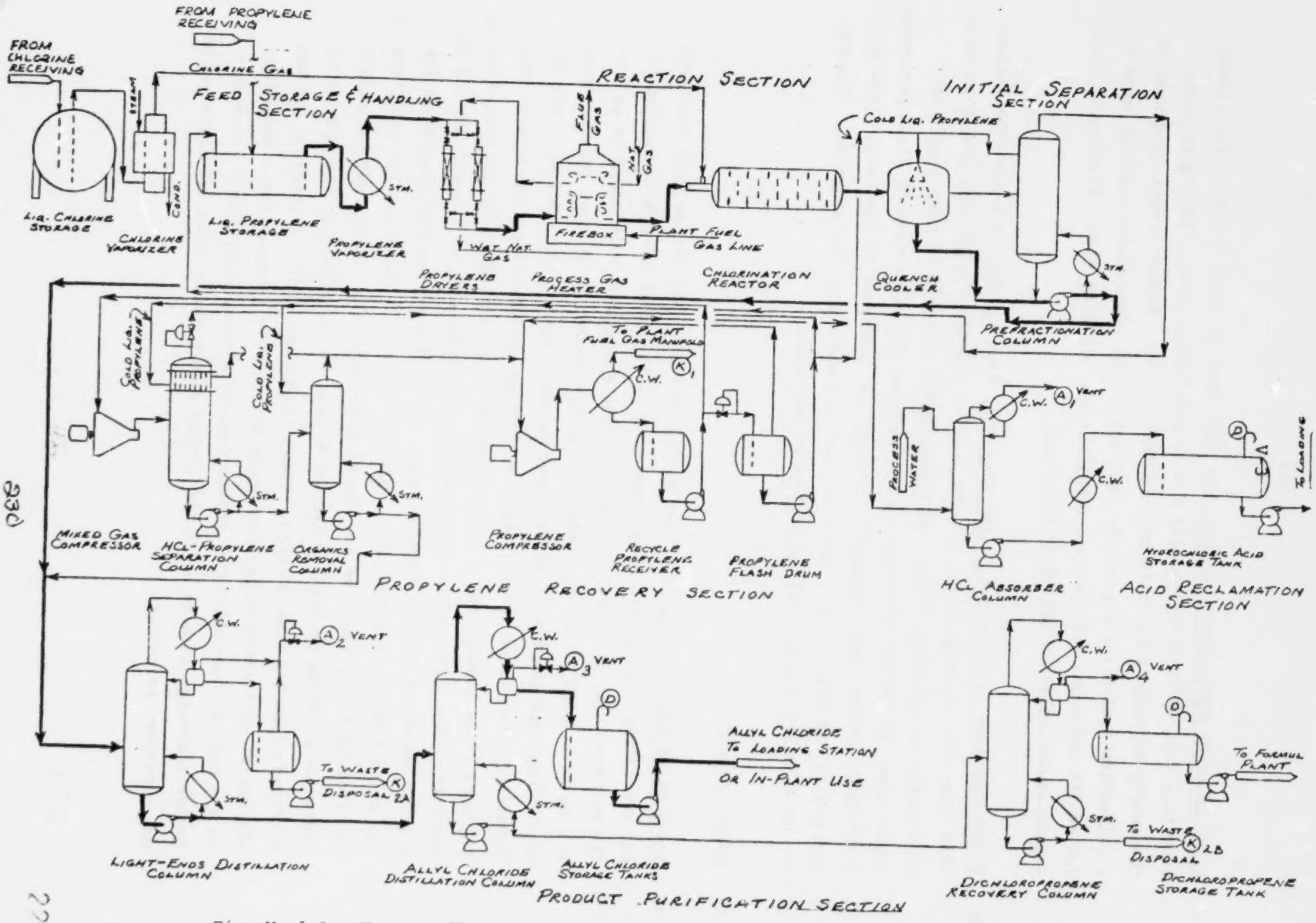
FROM CHLORINE RECEIVING
FROM PROPYLENE RECEIVING
CHLORINE GAS
FEED STORAGE & HANDLING SECTION
REACTION SECTION
INITIAL SEPARATION SECTION
STEAM
COND.
LIQ. CHLORINE STORAGE
CHLORINE VAPORIZER
LIQ. PROPYLENE STORAGE
PROPYLENE VAPORIZER
STM.
FLUE GAS
NAT. GAS
FIREBOX
WET NAT. GAS
PLANT FUEL GAS LINE
PROPYLENE DRYERS
PROCESS GAS HEATER
CHLORINATION REACTOR
COLD LIQ. PROPYLENE
QUENCH COOLER
PREFRACTIONATION COLUMN
COLD LIQ. PROPYLENE
COLD LIQ. PROPYLENE
TO PLANT FUEL GAS MANIFOLD
K 1
C.W.
A 1 VENT
PROCESS WATER
D
V
TO LOADING
MIXED GAS COMPRESSOR
HCL-PROPYLENE SEPARATION COLUMN
ORGANICS REMOVAL COLUMN
PROPYLENE COMPRESSOR
RECYCLE PROPYLENE RECEIVER
PROPYLENE FLASH DRUM
HCL ABSORBER COLUMN
HYDROCHLORIC ACID STORAGE TANK
ACID RECLAMATION SECTION
PROPYLENE RECOVERY SECTION
A 2 VENT
A 3 VENT
A 4 VENT
TO WASTE DISPOSAL
K 2A
ALLYL CHLORIDE TO LOADING STATION OR IN-PLANT USE
TO FORMUL PLANT
TO WASTE DISPOSAL
K 2B
LIGHT-ENDS DISTILLATION COLUMN
ALLYL CHLORIDE DISTILLATION COLUMN
ALLYL CHLORIDE STORAGE TANKS
DICHLOROPROPENE RECOVERY COLUMN
DICHLOROPROPENE STORAGE TANK
PRODUCT PURIFICATION SECTION

Fig. V-1.A. Uncontrolled Model-Plant Flowsheet for Production of Allyl Chloride

c. Allyl Chloride Distillation Column Vent (See Vent A_3, Fig. V-1.A)——The stream from this vent is relatively small and insignificant. For a 113-Gg/yr plant the hourly emission rate would be less than 1.3 kg. Either a vent condenser or a collection system for piping the vent gas to the plant flare could be used to reduce the emission, but the cost-benefit ratio would be high. Flaring of these vapors would result in HCl vapor emissions.

d. Dichloropropene Distillation Column Vent (See Vent A_4, Fig. V-1.A)——The stream from this vent is significant in size. For a 113-Gg/yr plant the hourly emission rate would be less than 13 kg. Dichloropropene is toxic in both liquid and vapor form; so the VOC emission must be reduced for protection of plant personnel. A scrubber system, vent condenser, or vent gas incineration (to collect the gas and pipe it to plant flare) could be used to reduce this VOC emission. Flaring of these vapors would result in HCl vapor emissions.

2. Epichlorohydrin

a. Epoxidation Reactor Vent (See Vent B, Fig. V-1.B)——The stream from this vent can constitute the largest single emission in the epichlorohydrin section of the process. For a 113-Gg/yr plant the hourly emission rate could be as low as 2.6 kg or as high as 260 kg. Emission levels depend on process design, operating conditions, and the alkali source used in the ring-closing reaction. Use of a carbonate (such as sodium carbonate or calcium carbonate) as the alkali source releases large quantities of carbon dioxide as a by-product of the ring-closing reaction. The large volume of carbon dioxide then acts as a sweep gas and carries a large amount of epichlorohydrin vapor along with the carbon dioxide as the gas exits from the reactor vent. The most effective technique for reduction of VOC from this vent would be the use of a noncarbonate alkali (such as sodium hydroxide solution or calcium hydroxide slurry) to neutralize the hydrochloric acid and close the epoxide ring. Other techniques that are possible include the use of activated-carbon adsorption or vent gas incineration. Depending on the cost of non-carbonate- versus carbonate-containing alkali, an alternative technolgy such as activated carbon adsorption or vent gas incineration may sometimes be cheaper.

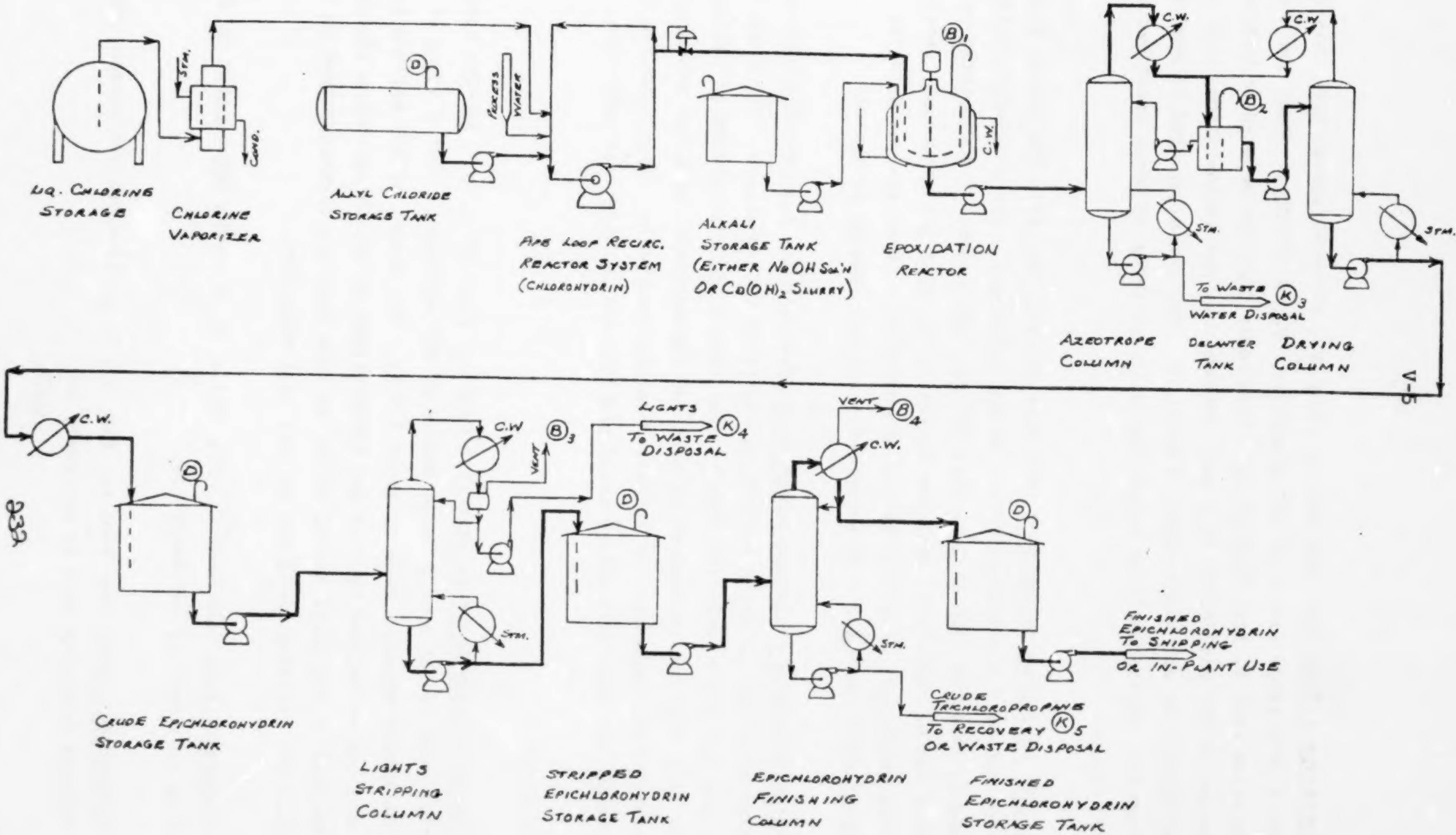
LIQ. CHLORINE STORAGE
STM.
CHLORINE VAPORIZER
COND.
D
ALLYL CHLORIDE STORAGE TANK
PROCESS WATER
PIPE LOOP RECIRC. REACTOR SYSTEM (CHLOROHYDRIN)
ALKALI STORAGE TANK (EITHER NaOH SOL'N OR Ca(OH)2 SLURRY)
B1
C.W.
EPOXIDATION REACTOR
C.W.
C.W.
B2
STM.
TO WASTE WATER DISPOSAL
K3
STM.
AZEOTROPE COLUMN
DECANTER TANK
DRYING COLUMN
C.W.
D
CRUDE EPICHLOROHYDRIN STORAGE TANK
C.W
B3
VENT
STM.
LIGHTS STRIPPING COLUMN
LIGHTS TO WASTE DISPOSAL
K4
D
STRIPPED EPICHLOROHYDRIN STORAGE TANK
VENT
B4
C.W.
STM.
EPICHLOROHYDRIN FINISHING COLUMN
CRUDE TRICHLOROPROPANE TO RECOVERY OR WASTE DISPOSAL
K5
D
FINISHED EPICHLOROHYDRIN STORAGE TANK
FINISHED EPICHLOROHYDRIN TO SHIPPING OR IN-PLANT USE

Fig. V-1.B. Uncontrolled Model-Plant Flowsheet for Production of Epichlorohydrin

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b. Azeotrope Column Vent (See Vent B_2, Fig. V-1.B)——The stream from this vent is not a very large source of VOC emissions. For a 113-Gg/yr plant the hourly emission rate is less than 10 kg. Techniques that can be used to reduce the amount of VOC emitted by this vent include vent gas incineration, vent gas scrubbing, or activated-carbon adsorption. Any technique used to remove VOC from this stream would be rather expensive in terms of money spent per unit of VOC reduced.

c. Lights Stripping Column Vent (See Vent B_3, Fig. V-1.B)——The stream from this vent can be a significant source of VOC emissions. For a 113-Gg/yr plant the hourly emission rate is less than 100 kg. The amount of VOC emitted by this vent can be reduced by vent gas incineration, vent gas scrubbing, refrigerated vent condenser, or activated-carbon adsorption. Vent gas incineration (flare) is probably the most cost-effective means for removal of the VOC.[5]

d. Epichlorohydrin Finishing Column Vent (See Vent B_4, Fig. V-1.B)——The stream from this vent is not a very large source of VOC emissions. For a 113-Gg/yr plant the hourly emission rate is less than 5 kg. The amount of VOC emitted by this vent can be reduced by vent gas incineration, vent gas scrubbing, refrigerated vent condenser, or activated-carbon adsorption. Any technique used to remove VOC from this stream would probably not be very cost effective.

3. Glycerin

a. Carbon Dioxide Absorber Vent (See Vent C_1, Fig. V-1.C, p. 1)——The stream from this vent is not a very large source of VOC emissions. For a 55-Gg/yr plant the hourly emission rate is about 2.5 kg. The amount of VOC emitted by this vent can be reduced by vent gas incineration or activated-carbon adsorption. Because of the small amount of VOC in this vent any technique used to reduce this VOC emission would not be very cost effective.

b. Evaporator Vent (See Vent C_2, Fig. V-1.C, p. 1)——The VOC content in the stream from this vent is extremely low.

c. Concentrator Vent (See Vent C_3, Fig. V-1.C, p. 1)——The VOC content in the gas emitted from this vent is extremely low.

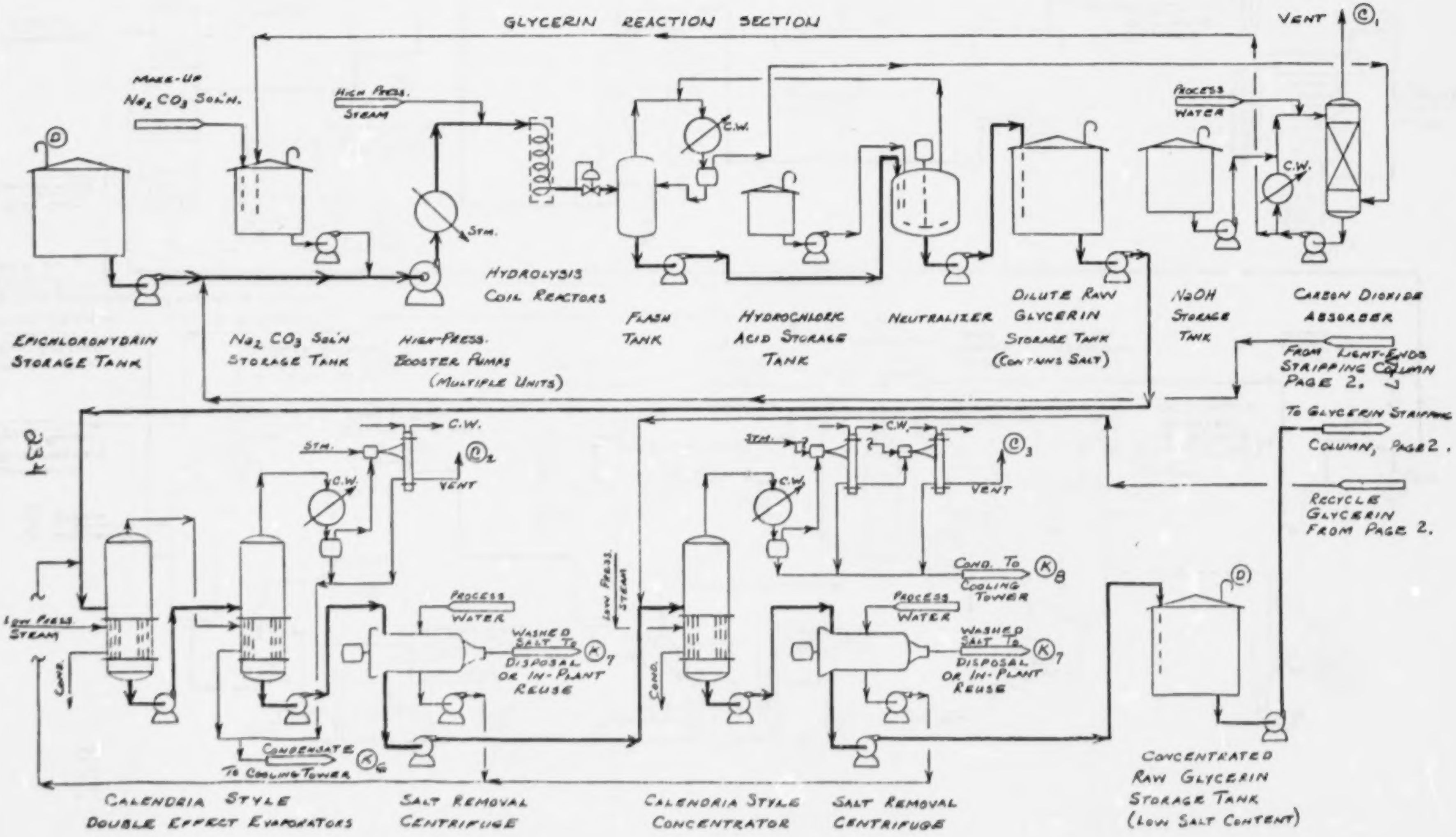
GLYCERIN REACTION SECTION
VENT
C1
MAKE-UP Na2 CO3 SOL'N.
HIGH PRESS. STEAM
PROCESS WATER
C.W.
C.W.
D
STM.
HYDROLYSIS COIL REACTORS
FLASH TANK
HYDROCHLORIC ACID STORAGE TANK
NEUTRALIZER
DILUTE RAW GLYCERIN STORAGE TANK (CONTAINS SALT)
NaOH STORAGE TANK
CARBON DIOXIDE ABSORBER
EPICHLOROHYDRIN STORAGE TANK
Na2 CO3 SOL'N STORAGE TANK
HIGH-PRESS. BOOSTER PUMPS (MULTIPLE UNITS)
FROM LIGHT-ENDS STRIPPING COLUMN PAGE 2.
TO GLYCERIN STRIPPING COLUMN, PAGE 2.
RECYCLE GLYCERIN FROM PAGE 2.
STM.
C.W.
C.W.
C2
VENT
STM.
C.W.
C.W.
C3
VENT
LOW PRESS. STEAM
LOW PRESS. STEAM
COND.
COND.
PROCESS WATER
PROCESS WATER
WASHED SALT TO DISPOSAL OR IN-PLANT REUSE
K7
WASHED SALT TO DISPOSAL OR IN-PLANT REUSE
K7
COND. TO COOLING TOWER
K8
CONDENSATE TO COOLING TOWER
K6
D
CALENDRIA STYLE DOUBLE EFFECT EVAPORATORS
SALT REMOVAL CENTRIFUGE
CALENDRIA STYLE CONCENTRATOR
SALT REMOVAL CENTRIFUGE
CONCENTRATED RAW GLYCERIN STORAGE TANK (LOW SALT CONTENT)

Fig. V-1.C. Uncontrolled Model-Plant Flowsheet for Production of Glycerin by the Chlorination Process

Page 1 of 2

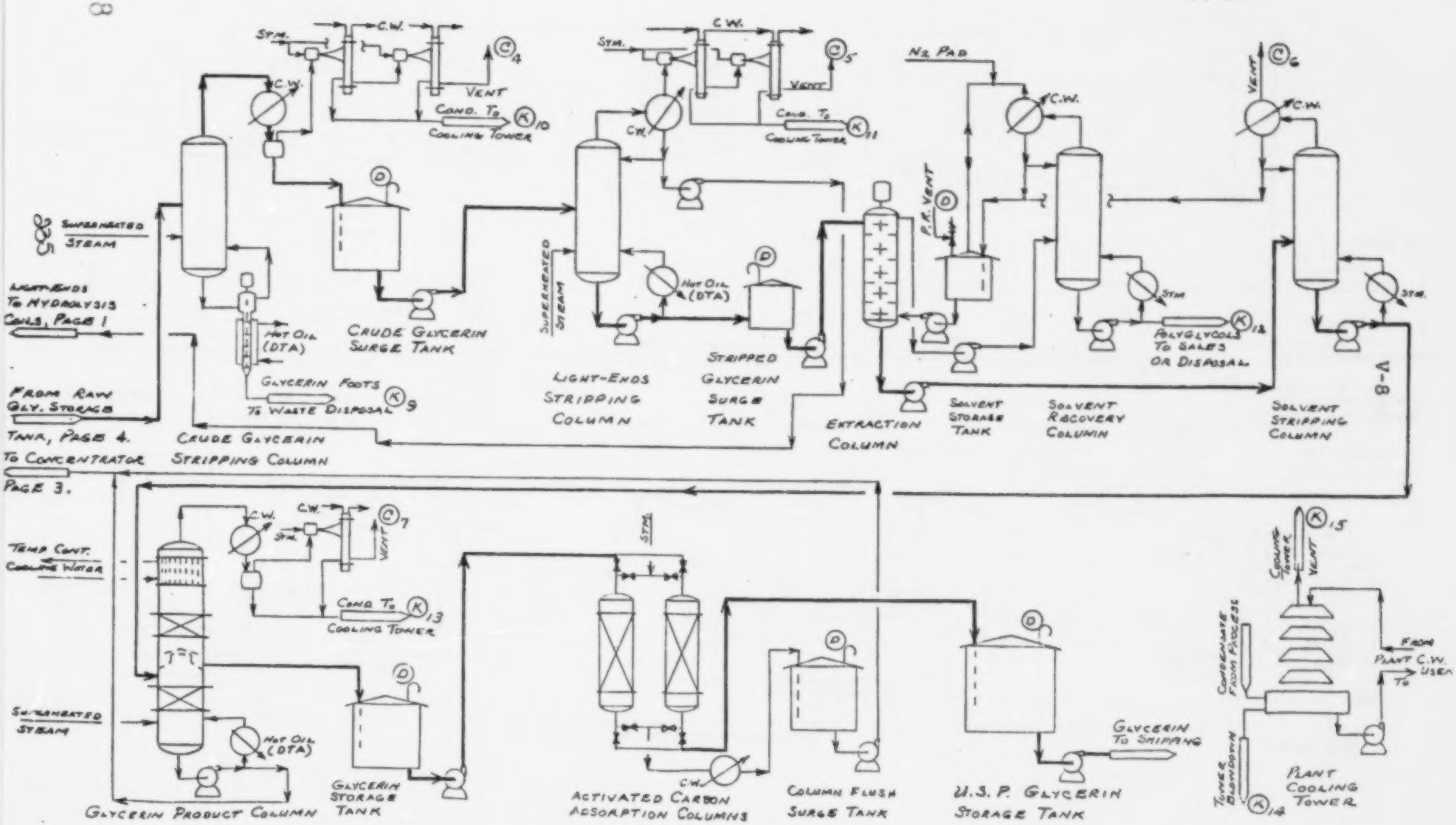
SUPERHEATED STEAM
LIGHT-ENDS TO HYDROLYSIS COILS, PAGE 1
FROM RAW GLY. STORAGE TANK, PAGE 4.
TO CONCENTRATOR PAGE 3.
STM.
C.W.
C.W.
©4
VENT
COND. TO COOLING TOWER
Ⓚ10
Ⓓ
HOT OIL (DTA)
GLYCERIN FOOTS TO WASTE DISPOSAL
Ⓚ9
CRUDE GLYCERIN SURGE TANK
CRUDE GLYCERIN STRIPPING COLUMN
STM.
C.W.
C.W.
©5
VENT
COND. TO COOLING TOWER
Ⓚ11
SUPERHEATED STEAM
HOT OIL (DTA)
Ⓓ
LIGHT-ENDS STRIPPING COLUMN
STRIPPED GLYCERIN SURGE TANK
P.R. VENT
Ⓓ
EXTRACTION COLUMN
N2 PAD
C.W.
SOLVENT STORAGE TANK
STM
POLYGLYCOLS TO SALES OR DISPOSAL
Ⓚ12
SOLVENT RECOVERY COLUMN
VENT
©6
C.W.
STM.
SOLVENT STRIPPING COLUMN
V-8
TEMP CONT. COOLING WATER
SUPERHEATED STEAM
C.W.
C.W.
STM.
©7
VENT
COND TO COOLING TOWER
Ⓚ13
HOT OIL (DTA)
GLYCERIN PRODUCT COLUMN
Ⓓ
GLYCERIN STORAGE TANK
STM.
C.W.
ACTIVATED CARBON ADSORPTION COLUMNS
Ⓓ
COLUMN FLUSH SURGE TANK
Ⓓ
U.S.P. GLYCERIN STORAGE TANK
GLYCERIN TO SHIPPING
COOLING TOWER
VENT
Ⓚ15
CONDENSATE FROM PROCESS
TOWER BLOWDOWN
Ⓚ14
FROM PLANT C.W. USER
TO
PLANT COOLING TOWER

Fig. V-1.C (Continued)

d. Stripping Column Vent (See Vent C_4, Fig. V-1.C, p. 2)——The VOC content in the stream from this vent is extremely low.

e. Light-Ends Column Vent (See Vent C_5, Fig. V-1.C, p. 2)——The VOC emitted from this vent is extremely low.

f. Solvent Stripping Column Vent (See Vent C_6, Fig. V-1.C, p. 2)——The VOC content in the stream from this vent is low. For a 55-Gg/yr plant the hourly emission rate is about 1.3 kg. The amount of VOC emitted by this vent can be reduced by vent gas incineration, vent gas scrubbing, refrigerated vent condenser, or activated-carbon adsorption. However, because of the small amount of VOC emitted, reduction techniques would not be very cost effective.

g. Product Column Vent (See Vent C_7, Fig. V-1.C, p. 2)——The VOC content in the gas from this vent is extremely low.

h. Cooling Tower (See K_{15}, Fig. V-1.C, p. 2)——The cooling tower emits a significant amount of VOC. For a 55-Gg/yr plant the hourly emission rate is about 17 kg of VOC, predominantly acetone. The main source of the VOC is the aqueous condensate from the water condenser on the product column. This contaminated water stream is used as part of the makeup water in the cooling tower. The acetone in the water stream from the product column has a low concentration and can best be eliminated by being steam stripped or vacuum stripped from the product column water condensate stream in a stripping-rectification column. In that way the recovered acetone could be recycled to the process. A cost-effectiveness study is needed to determine the cost associated with this method of reducing the VOC emission.

B. OXIDATION PROCESS[1,6]

Table V-2 summarizes the controlled emissions for the oxidation process.

1. Acrolein

a. Carbon Dioxide Stripping Tower Vent (See Vent A_1, Fig. V-2)——The stream from this vent is the largest single vent stream in the acrolein section of the oxidation process. For a 25-Gg/yr plant the hourly emission rate for VOC, principally

Table V-2. Controlled VOC Emissions for the Oxidation Process Model Plant

Process Step	Source	Stream Designation (Fig.III-2)	Control Technique	Emission Reduction (%)	Emission Ratio[a] (g/Mg)
Acrolein					
	Carbon dioxide stripping tower vent	A_1	Flare	98	120
	Aqueous acrolein receiver vent	A_2	Flare	98	60
	Distillation system receiver vent	A_3	Flare	98	150
Allyl alcohol					
	Catalyst preparation vent	B_1	Vent condenser	99	2250
	Filtration system vent	B_2	Scrubber	95	160
	Lights stripper column vent	B_3	Flare	98	220
	Distillation system vents (3)	B_4	None[b]	0	160
		B_5	Vent condenser	95	80
		B_6	Vent condenser	80	1900
Glycerin					
	Light ends stripper vent	C_1	Scrubber	97	450
	Concentrator column vent	C_2	None	0	150
	Glycerin flasher column vent	C_3	None	0	150
	Product column vent	C_4	None	0	150
	Furnace vent	C_5	None	0	150

[a] g of total VOC emissions per Mg of product produced.

[b] Process condenser keeps emissions low.

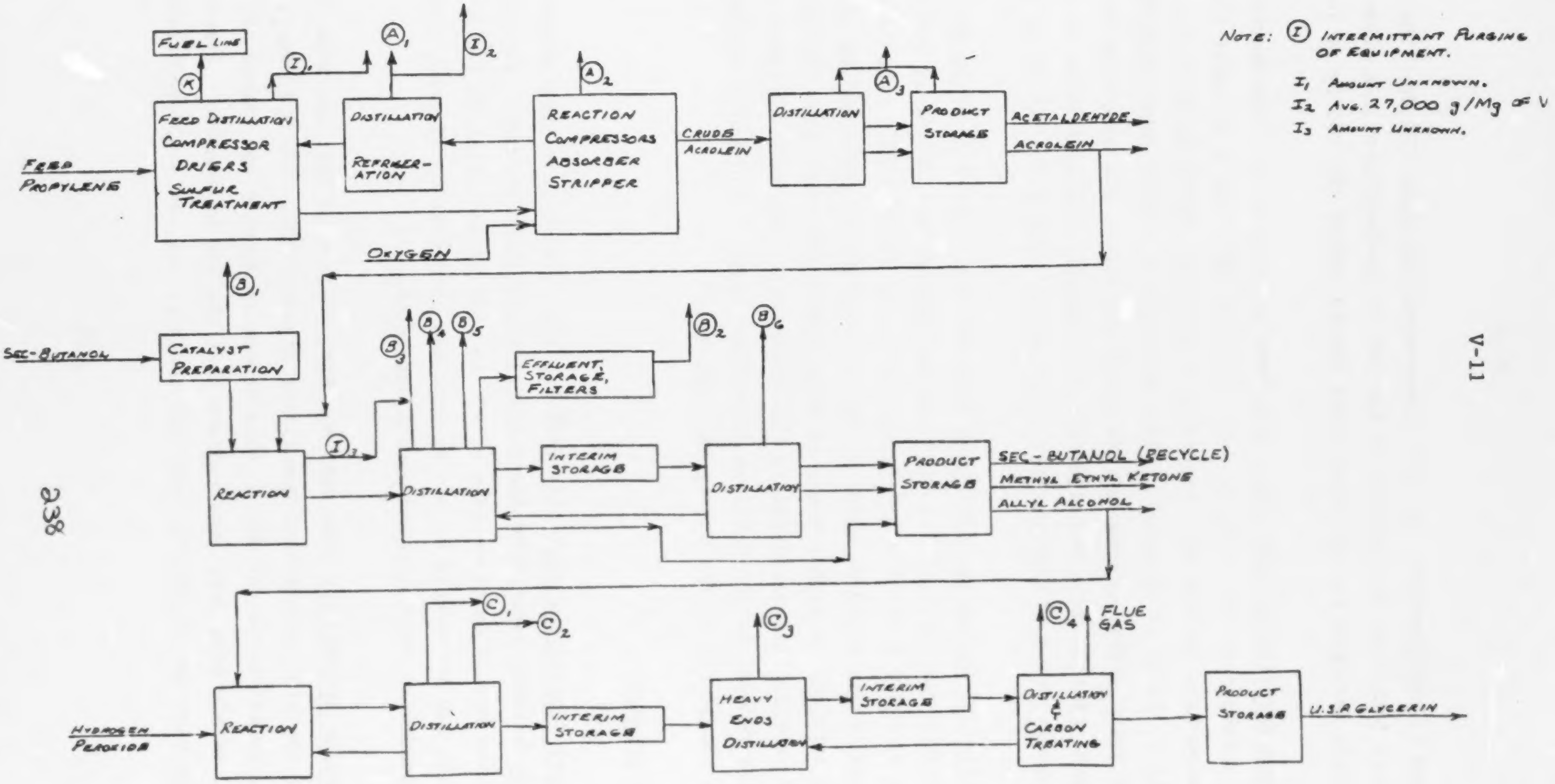
Note: Ⓘ Intermittant Purging of Equipment.
I_1 Amount Unknown.
I_2 Avg. 27,000 g/Mg of V
I_3 Amount Unknown.
Feed Propylene
Fuel Line
Ⓚ
Feed Distillation Compressor Driers Sulfur Treatment
$Ⓘ_1$
Distillation Refrigeration
$Ⓐ_1$
$Ⓘ_2$
Reaction Compressors Absorber Stripper
$Ⓐ_2$
Oxygen
Crude Acrolein
Distillation
$Ⓐ_3$
Product Storage
Acetaldehyde
Acrolein
Sec-Butanol
Catalyst Preparation
$Ⓑ_1$
Reaction
$Ⓘ_3$
Distillation
$Ⓑ_3$
$Ⓑ_4$
$Ⓑ_5$
Effluent, Storage, Filters
$Ⓑ_2$
Interim Storage
Distillation
$Ⓑ_6$
Product Storage
Sec-Butanol (Recycle)
Methyl Ethyl Ketone
Allyl Alcohol
Hydrogen Peroxide
Reaction
Distillation
$Ⓒ_1$
$Ⓒ_2$
Interim Storage
Heavy Ends Distillation
$Ⓒ_3$
Interim Storage
Distillation & Carbon Treating
$Ⓒ_4$
Flue Gas
Product Storage
U.S.P. Glycerin

Fig. V-2. Block Flowsheet of Oxidation Process for Uncontrolled Model Plant Producing Synthetic Glycerin

C_2 and C_3 hydrocarbons, in this stream would be about 175 kg. The most satisfactory technique for removal of the VOC is incineration in a plant flare. A properly designed and operated flare should reduce the VOC by at least 98%.[5]

b. Aqueous Acrolein Receiver Vent (See Vent A_2, Fig. V-2)——The discharge from the vent scrubber on the receiver vent contains VOC. For a 25-Gg/yr plant the hourly emission rate for the VOC, principally acrolein, would be about 8.5 kg (accompanied by about 162 kg of methane). Since acrolein is highly toxic in both liquid and vapor form, safety considerations would not permit its discharge to the atmosphere. The most satisfactory technique for its removal is incineration in a plant flare. A properly designed and operated flare should reduce the VOC by at least 98%.[5]

c. Distillation System Receiver Vent (See Vent A_3, Fig. V-2)——The discharge from the column receivers on the distillation system is a source of VOC emissions. For a 25-Gg/yr plant the hourly emission rate for the VOC, principally acrolein, in this stream would be about 21 kg (accompanied by about 400 kg of methane). Since acrolein is highly toxic in both liquid and vapor form, safety considerations would prohibit its discharge to the atmosphere. The most satisfactory technique for its removal is incineration in a plant flare. A properly designed and operated flare should reduce the VOC by at least 98%.[5]

2. Allyl Alcohol

a. Catalyst Preparation Vent (See Vent B_1, Fig. V-2)——This vent discharges hydrogen and sec-butanol vapor from the catalyst preparation reactor. For a 25-Gg/yr plant the hourly emission rate of VOC in this stream is about 640 kg. The VOC emission can be reduced by use of vent gas incineration (flare), scrubber vent, vent condenser, or activated-carbon adsorption.[4,5]

b. Filtration System Vent (See Vent B_2, Fig. V-2)——The vent gas from the filtration system contains significant quantities of toxic VOC. For a 25-Gg/yr plant the hourly emission rate of VOC in this stream is about 9 kg. Since the vapors are toxic, safety considerations require that the VOC be removed. Removal techniques include vent gas scrubbing, vent gas incineration, or activated-carbon adsorption.[4,5]

c. Lights Stripper Column Vent (See Vent B_3, Fig. V-2)——The vent stream from this column system is a large and significant vent stream in the allyl alcohol section of the oxidation process. For a 25-Gg/yr plant the hourly rate of VOC emissions in this stream is about 31 kg (accompanied by about 31 kg of methane). The VOC emitted by this vent is about 50% acrolein, which is highly toxic in both vapor and liquid form. Safety considerations require that this toxic VOC be removed. Removal techniques include vent gas incineration (to flare), refrigerated vent condenser, vent gas scrubbing, or activated-carbon adsorption.[4,5]

d. Distillation System Column Vents (See Vents B_4, B_5, and B_6, Fig. V-2)——There are three individual vents from the distillation system columns and each one contains significant quantities of VOC. For a 25-Gg/yr plant the hourly rate of VOC emissions from these three vents is 0.46 kg, 4.6 kg, and 27 kg, respectively. The VOC can be removed from these vent streams by vent condensers, vent gas incineration, vent gas scrubbing, or activated-carbon adsorption.[4,5]

3. Glycerin

a. Light-Ends Stripper Vent (See Vent C_1, Fig. V-2)——The gas stream from this vent is the largest and only significant VOC process emission stream in the glycerin section of the oxidation process. For a 25-Gg/yr plant the hourly rate of VOC emissions from this vent is about 43 kg. This VOC stream contains acrolein and allyl alcohol, which are toxic in both liquid and vapor form and therefore for safety considerations must be removed. They can be removed by a vent condenser, a vent gas scrubber, vent gas incineration, or activated-carbon adsorption.[4,5]

b. Concentrator Column Vent (See Vent C_2, Fig. V-2)——The VOC content of the gas emitted by this vent is extremely low.

c. Glycerin Flasher Column Vent (See Vent C_3, Fig. V-2)——The VOC content of the stream from this vent is very low.

d. Product Column Vent (See Vent C_4, Fig. V-2)——The VOC content in the gas emitted by this vent is very low.

e. Furnace Vent (See Vent C_5, Fig. V-2)——The VOC content in the stream from this vent is very low.

C. OXIDATION PROCESS VARIATION (ACROLEIN ONLY)[1,7]

The controlled emissions for this oxidation process variation are summarized in Table V-3.

1. Acrolein Absorber Vent

This stream from this vent is a source of an extremely large and significant VOC process emission. For a 25-Gg/yr plant the hourly rate of VOC emissions from this source is about 360 kg. Acrolein constitutes about 40% of the total VOC. Since acrolein is a highly toxic material in both liquid and vapor form, safety considerations require its removal from the vent stream. The VOC can be removed by vent gas incineration or activated-carbon adsorption.[5]

Table V-3. Controlled VOC Emissions for the Union Carbide Variation of the Oxidation Process (Acrolein Only)

Source	Stream Designation	Control Technique	Emission Reduction (%)	Emission Ratio* (g/Mg)
Acrolein absorber vent	1	Thermal oxidation	99	1260
Combined distillation system vent header	2a-e	Flare	98	760

*g of total VOC emission per Mg of acrolein produced.

2. Combined Distillation System Vent Header

This stream from this vent is a significant source of VOC process emissions. For a 25-Gg/yr plant the hourly rate of VOC emissions, principally acrolein, from this source is about 109 kg. Since acrolein is a highly toxic material in both liquid and vapor from, safety considerations require that it be removed from this vent stream. The VOC can be removed by vent gas incineration (in-plant flare), refrigerated vent condensers, vent scrubbers, or activated-carbon adsorption.[4,5]

D. ISOMERIZATION PROCESS

No data are currently available on emissions for this process, and so no estimates on emission reduction techniques or possible amounts of emission reduction can be made.

E. REFERENCES*

1. R. G. Muller, Glycerin and Intermediates, Report No. 58, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (December, 1969).

2. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Shell Chemical Co. Process at Deer Park, TX, Jan. 25, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Dow Chemical Co. Process at Freeport, TX, Jan. 26 and 27, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

4. D. Erikson, IT Enviroscience, Inc., Control Device Evaluation--Condensation, in preparation.

5. V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation--Flares and Boilers, in preparation.

6. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Shell Chemical Co. Process at Norco, LA, Jan. 25, 1978 (on file at EPA, ESED, Research Triangle Park, NC)

7. F. D. Best, Union Carbide Corp., Taft, LA, letter to EPA, Apr. 21, 1978, in response to EPA request for information on the Union Carbide acrolein process.

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

VI. IMPACT ANALYSIS

A. CONTROL COST IMPACT

No estimates of control costs or cost effectiveness have been prepared for this abbreviated report.

B. ENVIRONMENTAL IMPACTS

1. Chlorination Process[1,2]

Table VI-1 lists the environmental impact of reduced VOC emissions by application of the described control systems to the chlorination process for synthetic glycerin and/or intermediates.

2. Oxidation[3]

Table VI-2 gives the environmental impact of reduced VOC emissions by application of the described control systems to the oxidation process for synthetic glycerin and/or intermediates.

3. Oxidation Process Variation (Acrolein Only)[4]

Table VI-3 shows the environmental impact of reduced VOC emissions by application of the described control systems to the oxidation process for synthetic acrolein.

4. Isomerization Process

No information is available at present to permit the estimation of environmental impacts from this process.

C. SUMMARY

The emission estimates for the various model plants are summarized in Table VI-4 in terms of controlled versus uncontrolled emissions based on SRI data for 1977 production levels.[1—7]

Since most of the emissions produced in the manufacture of glycerin intermediates (such as allyl chloride, epichlorohydrin, acrolein, allyl alcohol, etc.) are volatile and toxic organics, safety requirements dictate that they be controlled to protect operating personnel. Because of the safety hazards and the resultant

Table VI-1. Environmental Impact from Controlled Chlorinated Process Model Plant

Process Step	Source	Stream Designation (Figs.III-1.A—C)	Control Technique	Emission Reduction (%)	Emission Reduction Ratio(g/Mg)*
Allyl chloride (Fig.III-1.A)	HCl absorber vent	A_1	None	0	0
	Light-ends dist. column vent	A_2	Flare	98	980--1370
	Allyl chloride dist. column vent	A_3	None	0	0
	Dichloropropene dist. column vent	A_4	Scrubber	50	Up to 500
Epichlorohydrin (Fig.III-1.B)	Epoxidation reactor vent	B_1	Use of NaOH or $Ca(OH)_2$	99	19,800
	Azeotrope column vent	B_2	Scrubber	84	Up to 670
	Lights stripping column vent	B_3	Flare	98	Up to 7840
	Finishing column vent	B_4	None	0	0
Glycerin (Fig.III-1.C, pp. 1,2)	Carbon dioxide absorber vent	C_1	None	0	0
	Evaporator vent	C_2	None	0	0
	Concentrator vent	C_3	None	0	0
	Stripping column vent	C_4	None	0	0
	Light-ends column vent	C_5	None	0	0
	Solvent stripping column vent	C_6	None	0	0
	Product column vent	C_7	None	0	0
	Cooling tower	K_{15}	Steam stripper	95	2660

*g of VOC emission reduced per Mg of product produced.

Table VI-2. Environmental Impact from Controlled Oxidation Process Model Plant

Process Step	Source	Stream Designation	Control Technique	Emission Reduction (%)	Emission Reduction Ratio(g/Mg)[a]
Acrolein	Carbon dioxide stripping tower vent	A_1	Flare	98	59,800
	Aqueous acrolein receiver vent	A_2	Flare	98	2940
	Distillation system receiver vent	A_3	Flare	98	7350
Allyl alcohol	Catalyst preparation vent	B_1	Vent condenser	99	223,000
	Filtration system vent	B_2	Scrubber	95	3000
	Lights stripper column vent	B_3	Flare	98	10,800
	Distillation system vents (3)	B_4	None[b]		
		B_5	Vent condenser	90	1440
		B_6	Vent condenser	80	7600
Glycerin	Light-ends stripper vent	C_1	Scrubber	97	14,500
	Concentrator column vent	C_2	None		
	Glycerin flasher column vent	C_3	None		
	Product column vent	C_4	None		
	Furnace vent	C_5	None		

[a] g of total VOC emission reduced per Mg of product produced.

[b] Process condenser keeps emissions low.

Table VI-3. Environmental Impact from Controlled Oxidation Process Variation (Acrolein Only)

Source	Stream Designation	Control Technique	Emission Reduction (%)	Emission Reduction Ratio (g/Mg)*
Acrolein absorber vent	1	Thermal oxidation	99	124,700
Combined distillation system vent header	2a-e	Flare	98	37,500

*g of total VOC emission reduced per Mg of product produced.

Table VI-4. Comparison of Controlled and Uncontrolled Emissions in the Synthesis of Glycerin and/or Intermediates at 1977 Production Levels

Process	Product	Estimated 1977 Production (Gg/yr)	Emission Ratio (g/Mg)[a]		Emission Rate (kg/hr)	
			Uncontrolled	Controlled	Uncontrolled	Controlled
Chlorination	Allyl chloride	132	61,250	1,950	923	29.4
	Epichlorohydrin	132	29,200	890	440	13.4
	Glycerin	29.5	3,900	1,240	13	4.2
Oxidation	Acrolein	10.6	71,500	330	86.5	0.4
	Allyl alcohol	9.8	250,500	4,770	280.2	5.3
	Glycerin	13.6	15,600	1,050	24.2	1.6
Oxidation variation	Acrolein	9.8	164,300	2,020	184	2.3
Isomerization	Allyl alcohol	11.2	Unknown	Unknown	Unknown	Unknown
	Peracetic acid	15.1[b]	Unknown	Unknown	Unknown	Unknown
	Glycerin	15.9	Unknown	Unknown	Unknown	Unknown

[a] g of total VOC emission per Mg of product produced.

[b] Additional peracetic acid is produced for use in other processes.

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emission control, most production facilities for the manufacture of synthetic glycerin and/or the intermediates produce emissions similar to those listed for the applicable controlled model plant. Process emission estimates for the entire domestic production of synthetic glycerin and its intermediates are presented in Table VI-4 for 1977. By counting the intermediates as separate products, the total production for 1977 was estimated to be 338 Gg, with process VOC emissions constituting 490 Mg. Even though no growth is projected for synthetic glycerin, some of the intermediates do have significant growth rates. Based on projected growth rates, the 1979 emission level is estimated to be 537 Mg. The VOC emissions estimate does not include fugitive, secondary, or storage emissions, which are expected to be lower than typical for the SOCMI because of toxic considerations. Since the emission ratios for the isomerization process are not known, production quantities and emissions for this process are not included in the above estimates.

D. REFERENCES*

1. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Shell Chemical Co. Process at Deer Park, TX, Jan. 25, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Dow Chemical Co. Process at Freeport, TX, Jan. 26 and 27, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Shell Chemical Co. Process at Norco, LA, Jan. 25, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

4. F. D. Best, Union Carbide Corp., Taft, LA, letter to EPA, Apr. 21, 1978, in response to EPA request for information on the Union Carbide acrolein process.

5. D. Oosterhof, "Glycerin," pp. 662.5021A—662.5023E in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (May 1978).

6. J. L. Blackford, "Epichlorohydrin," pp. 642.3021A—E and 642.3022A—V in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (May 1978).

7. S. L. Soder and K. L. Ring, "Propylene," pp. 300.5405E—300.5405L and 300.5405Q—300.5405R in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (August 1978).

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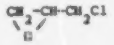
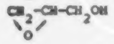
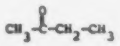
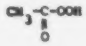
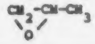
*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

Table A-1. Physical Properties of Organic Raw Materials, Intermediates, End Products, and By-Products[a]

Product Name	Molecular Formula	Molecular Weight	Boiling Point (°C)	Melting Point (°C)	Vapor Pressure (Pa)	Specific Gravity	Solubility in Water	Toxicity: Oral LD_{50} (Rat) (g/kg)	Toxicity: Vapor LC_{50} (Rat) (4 hr at g/Gg)[b]	Remarks
Acetaldehyde	CH_3-CHO	44.05	20.4	-123.5	1. X 10^5 at 20°C	0.78	Infinite			Extremely flammable
Acetic acid	CH_3-COOH	60.05	118.1	16.6		1.05	Infinite			Irritating, toxic, flammable at high concentration
Acrolein	$CH_2=CH-CHO$	56.06	52.7	-87.7	2.8 X 10^4 at 20°C	0.84	28%	0.046	8	Highly toxic, very reactive, lacrimator, highly flammable
Allyl alcohol	$CH_2=CH-CH_2OH$	58.08	97.2	-129	2.3 X 10^3 at 20°C	0.85	Infinite	0.064	165	Highly toxic, lacrimator, reactive, contact poison, flammable
Allyl chloride	$CH_2=CH-CH_2Cl$	76.53	44.6	-134.5	3.9 X 10^4 at 20°C	0.94	0.3%			Toxic, irritating vapors, contact poison, highly flammable
sec-Butanol	$CH_3-CHOH-CH_2-CH_3$	74.12	99.4	-114.7		0.80	11%	6.48		Toxic, flammable
sec-Butanone	$CH_3-CO-CH_2-CH_3$	72.10	79.6	-86.9		0.80	27%			Highly flammable
Dichlorohydrin	$CH_2Cl-CHOH-CH_2Cl$	128.99	174.3	< -20		1.37	11%			Toxic, vapors irritating and toxic, contact poison
	$CH_2Cl-CHCl-CH_2OH$		182			1.36	13%			Toxic, vapors irritating and toxic, contact poison
Dichloropropene	$C_3H_4Cl_2$ (mixture)	110.98			4.7 X 10^3 at 21°C	1.2	4%	0.140	1000	Highly toxic, pungent garlic odor
Epichlorohydrin	 $\underset{\diagdown O \diagup}{CH_2-CH}-CH_2Cl$	92.53	116.1	-57.1	2.3 X 10^3 at 25°C	1.18	6%	0.1--0.2		Toxic, vapors irritating and toxic, contact poison, sensitizer
Glycerin	$CH_2OH-CHOH-CH_2OH$	92.09	290	18		1.26	Infinite	27.5		
Glycidol	 $\underset{\diagdown O \diagup}{CH_2-CH}-CH_2OH$	74.08	166-7			1.11	Infinite			Toxic, reactive
Met.../l ethyl ketone	 $CH_3-\overset{O}{\overset{\parallel}{C}}-CH_2-CH_3$	72.2	79.6	-86.35	1.2 X 10^4 at 20°C	0.8054	Very soluble	3.4		
Peracetic acid	 $CH_3-\underset{\underset{O}{\parallel}}{C}-OOH$	76.05	105	0.1		1.23	Very soluble			Reactive, flammable, can explode if heated or contaminated
Propylene	$CH_2=CH-CH_3$	42.08	-47.7	-185		0.609[c]	0.085%			Flammable gas
Propylene oxide	 $\underset{\diagdown O \diagup}{CH_2-CH}-CH_3$	58.08	35			0.83	25%			Reactive, extremely flammable

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[a] The data in this table were abstracted from the sources listed on p. A-4.

[b] g of concentration per Gg of air.

[c] At -47°C.

Sources for Data Given in Table A-1:

1. Handbook of Chemistry and Physics, 45th ed., pp. C75--C601, edited by R. C. Weast *et al*., The Chemical Rubber Co., Cleveland, Ohio, 1964.

2. Handbook of Chemistry, 9th ed., pp. 384—721, edited by N. A. Lange *et al*., Handbook Publishers, Inc., Sandusky, Ohio, 1956.

3. Chemical Safety Data Sheet SD-99, Allyl Chloride, Manufacturing Chemists Association, Washington, D.C., 1973.

4. Epichlorohydrin—The Versatile Intermediate, Product Bulletin, Dow Chemical Co., Freeport, TX, 1975.

5. Physical Properties of Glycerine and Its Solutions, Product Bulletin, Dow Chemical Co., Freeport, TX (nd).

6. J. Dorigan, B. Frieler, and R. Duffy, "Methyl Ethyl Ketone," pp AIII-192, 193 in Scoring of Organic Air Pollutants, Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F-N, MTR-7248, Rev. 1, App. III (September 1976).

7. Acetaldehyde; Acrolein; Allyl Alcohol; s-Butyl Alcohol/2-Butanol; Dichloropropene-Dichloropropane, DD; Glycerine/Glycerol, Material Safety Data Sheets, Shell Chemical Co., Norco, LA (nd).

A. EXISTING PLANT CHARACTERIZATION

Information has been received regarding control devices or techniques from the following three manufacturers, covering three processes for the manufacture of intermediates and two processes for conversion of intermediates to synthetic glycerin:

1. The Chlorination Process

a. The Dow Chemical Co., Freeport, TX, has a nominal capacity for 113.4 Gg/yr of crude epichlorohydrin and a nominal capacity of 54.4 Gg/yr of synthetic glycerin. The information available on this plant is summarized in Table B-1.[1]

b. The Shell Chemical Co. has a nominal capacity of 49.9 Gg/yr of crude epichlorohydrin at each of two plants, Deer Park, TX, and Norco, LA. The combined nominal capacity of both plants for the manufacture of synthetic glycerin was stated to be 45.4 Gg/yr (including the capacity to manufacture glycerin via the acrolein route).[2] The information available on these plants is summarized in Table B-1.

2. The Oxidation Process

a. The Shell Chemical Co. has a nominal capacity of 24.9 Gg/yr of acrolein at the Norco, LA plant.[3] Total capacity for manufacture of synthetic glycerin is 45.4 Gg/yr, as stated in item 1.b.

b. The Union Carbide Corporation has a nominal capacity of 27.2 Gg/yr of acrolein at the Taft, LA, plant, with no capacity for conversion of acrolein to glycerin.[4] The information available on this plant is summarized in Table B-1.

B. RETROFITTING CONTROLS

The control devices and techniques discussed in Section V may not be applicable to existing plants. Retrofitting control devices or techniques into existing plants brings up such questions as: Is there space in the existing plant to fit in and install the new hardware required? Do the operating characteristics of the emission control device fit the operating characteristics of the process equipment? Are the operating characteristics and design limitations of the

Table B-1. Control Devices and Techniques Currently Used in Synthesis of Glycerin and/or Intermediates

				Control Device or Technology		
Process	Process Step	Source	Stream Designation[a]	By Dow	By Shell	By Union Carbide
Chlorination[a]	Allyl chloride	HCl absorber vent	A_1	Flare	Flare	
		Light-ends distillation column vent	A_2	Flare	Vent condenser	
		Allyl chloride dist. column vent	A_3	Flare	None	
		Dichloropropene dist. column vent	A_4	NR (not reported)	Scrubber	
	Epichlorohydrin	Epoxidation reactor vent	B_1	Thermal oxidizer	Use of NaOH or $Ca(OH)_2$	
		Azeotrope column vent	B_2	Thermal oxidizer	Scrubber	
		Lights stripping column vent	B_3	None	Scrubber	
		Finishing column vent	B_4	None	Scrubber	
	Glycerin	Carbon dioxide absorber vent	C_1	None	NR	
		Evaporator vent	C_2	None	NR	
		Concentrator vent	C_3	None	NR	
		Stripping column vent	C_4	None	NR	
		Light-ends column vent	C_5	None	NR	
		Solvent stripping column vent	C_6	None	NR	
		Product column vent	C_7	None	NR	
		Cooling tower	K_{15}	None	NR	
Oxidation[b]	Acrolein	Carbon dioxide stripping tower vent	A_1		Flare	
		Aqueous acrolein receiver vent	A_2		Flare	
		Distillation system receiver vent	A_3		Flare	
	Allyl alcohol	Catalyst preparation vent	B_1		Vent condenser	
		Filtration system vent	B_2		Scrubber	
		Lights stripper column vent	B_3		Flare	
		Distillation system vents (3)	B_4		None[c]	
			B_5		Vent condenser	
			B_6		Vent condenser	
	Glycerin	Light-ends stripper vent	C_1		Scrubber	
		Concentrator column vent	C_2		None	
		Glycerin flasher column vent	C_3		Vent condenser	
		Product column vent	C_4		None	
		Furnace vent	C_5		None	
Oxidation process variation[d]	Acrolein	Acrolein absorber vent	1			Thermal oxidizer
		Combined dist. system vent header	2a-e			Flare

[a] See Figs. V-1.A—C.

[b] See Fig. V-2.

[c] Process condenser keeps emissions low.

[d] No figure available.

control device compatible with the upset or emergency conditions that might be encountered with the process? Are the startup and shutdown characteristics of the control device compatible with the startup and shutdown requirements of the process? Are extensive process modifications needed to accomplish significant emission reductions? When changes in feedstock or intermediates are needed to reduce process emissions, are the changed feedstocks or intermediates readily available at reasonable prices?

The specific plants investigated for this report seem to have most of their emission sources fairly well controlled by either specific control devices or operating techniques. No specific recommendations for retrofitting additional controls or techniques are provided in this report.

C. REFERENCES*

1. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Dow Chemical Co. Process at Freeport, TX, Jan. 26 and 27, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Shell Chemical Co. Process at Deer Park, TX, Jan. 25, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. C. A. Peterson, IT Enviroscience, Inc., Trip Report Covering Discussion of Shell Chemical Co. Process at Norco, LA, Jan. 25, 1978 (on file at EPA, ESED, Research Traingle Park, NC).

4. F. D. Best, Union Carbide Corp., Taft, LA, Letter to EPA, Apr. 21, 1978, in response to EPA request for information on the Union Carbide acrolein process.

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REPORT 4

ACRYLIC ACID AND ESTERS

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VI-2	Net Annual Cost vs. Plant Capacity - Liquid-Fume Thermal Oxidation	VI-5
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D-1	Precision of Capital Cost Estimates	D-1

ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^1
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^2
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^4
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^1
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^9	1 Gg = 1 X 10^9 grams
M	mega	10^6	1 Mg = 1 X 10^6 grams
k	kilo	10^3	1 km = 1 X 10^3 meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

Acrylic acids and esters include three major categories of chemicals: acrylic acid, lower esters (methyl, ethyl, and butyl), and heavy esters (2-ethylhexyl and others). There are several processes for each of these categories. This report is organized so that the products in each category is considered a product in itself. However, the materials are produced at an integrated plant and may share common storage tank equipment and/or control devices. A model plant utilized to project organic emissions is based on an integrated acrylates production facility.

A. ORGANIC COMPOUNDS PRODUCED

1. Acrylic Acid (AA)

Acrylic acid production was selected for in-depth study because preliminary estimates indicated that total emissions of volatile organic compounds (VOC), excluding methane, are relatively high and that the product growth rate is expected to be higher than the industry average.[1]

Acrylic acid is a colorless liquid at ambient conditions (see Appendix A for pertinent physical properties). Compounds that are reported as organic emissions in relation to AA production are formaldehyde, formic acid, ethylene, acetaldehyde, acetic acid, propane, propylene, acetone, propionaldehyde, acrolein, ethyl acrylate, and others.[1--3] Since a variety of solvents may be used in AA production,[1] there may be additions or exceptions to these organic compounds, depending on the manufacturer's specific process.

2. Lower Esters

Methyl, ethyl, and butyl acrylates (MA, EA, and BA) were selected because preliminary estimates indicated that total emissions of VOC are relatively high, that the product growth is expected to be higher than the industry average, and that the production of acrylate esters is closely tied to acrylic acid production.[1]

MA, EA, and BA are colorless liquids possessing unusually potent odor properties. This has required producers to implement control devices to achieve emission reductions greater than usual for the synthetic organic chemicals industry.

3. Heavy Esters

A number of esters have molecular weights that are higher than those of MA, EA, and BA. They are called heavy esters and include 2-ethylhexyl acrylate (2-EHA) among others. Some producers consider BA a heavy ester. The heavy esters are normally liquids at ambient conditions (see Appendix A for pertinent physical properties). Compounds emitted from heavy-ester production include AA, MA, EA, and BA and its corresponding heavy alcohol, e.g., 2-ethylhexyl alcohol in the production of 2-EHA.

B. USAGE AND GROWTH OF ACRYLIC ACID AND ESTERS

Table II-1 shows the end uses and growth of acrylic acid and esters. The predominant end use is the manufacture of polymers for use in surface coatings, textiles, paper, polishes, leather, and other materials.[4] Small amounts of AA are used in the production of water-soluble resins and as a co-monomer for other polymers. A small amount of esters is used in the manufacture of acrylic fibers.[4]

The U.S. AA and ester capacity for 1976 was reported to be 618 Gg of total acrylate (including a recent major expansion). No data are available on the breakdown of the capacity of acrylate esters. About 66% of the 618 Gg of domestic capacity uses catalytic oxidation technology to oxidize propylene to acrylic acid. The remainder uses both a high- and a low-pressure modified Reppe process, starting with acetylene, for acrylic acid manufacture.[4] Recent announcements confirm a new propylene oxidation plant to be built in 1981 with an acrylic acid capacity of 59 Gg/yr.[5]

As of 1976 there were four U.S. producers of acrylic acid and esters. Table II-2 gives the producers and the processes used for the plant locations, shown in Fig. II-1. Most production facilities react acrylic acid with alcohol to form the lower and heavy esters at the same site at which the acrylic acid is produced. An exception to this is the Celanese Chemical Co., which transports about 12 Gg per year of AA from its Clear Lake, TX, plant to its Pampa, TX, plant, where the lower and heavy esters are made.[4] Another is the old Rohm

Table II-1. Acrylic Acid and Esters Usage and Growth*

End Use	Percent of Production (1976)	Average Annual Percent Growth (1974-1980)
Acrylic acid		
Esters	86	10 - 12
Other	14	7
Overall		9.5 - 11.3
Acrylates		
Emulsion polymers	75	6.8 - 8.2
Other	25	8.7
Overall		7.1 - 8.4

*See ref 4.

Table II-2. Acrylic Acid and Ester Capacity[a]

Producer	1976 Capacity[b] (Gg/yr)	Process	
		Acrylic Acid	Esters
Celanese Chemical Company			
Clear Lake, TX	138.5	c	d
Pampa, TX	Included above	None	d
Dow Badische Co.			
Freeport, TX	25.9[e]	f	g
Rohm and Haas Co.			
Deer Park, TX	181.6	None	h
	181.6	c	g
Union Carbide Corp.			
Taft, LA	90.8	c	g
Total	618.4		

[a] See ref 4.

[b] Based on total acrylates, i.e., acrylic acid plus esters.

[c] Propylene oxidation to acrylic acid.

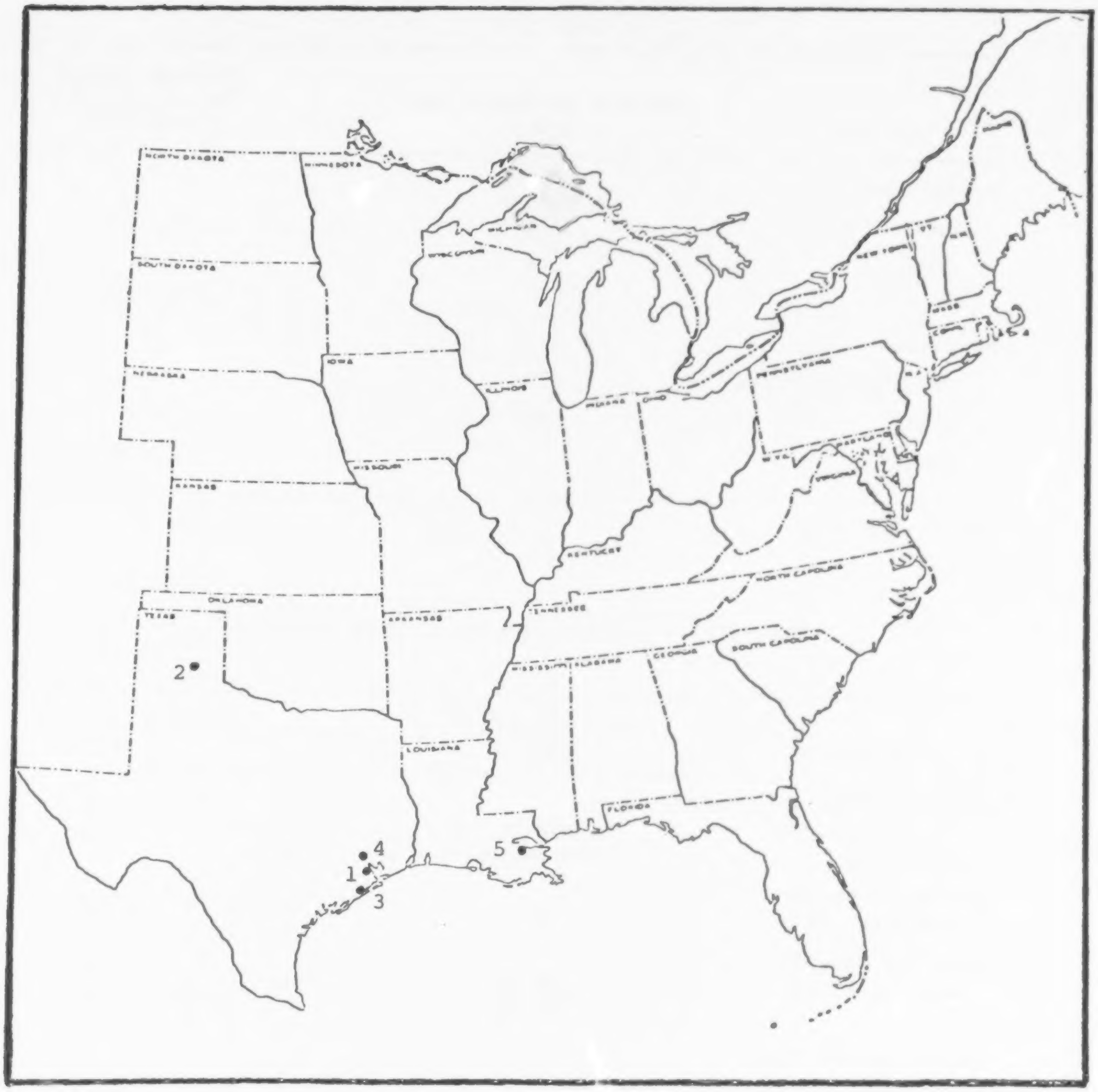
[d] Unknown confidential processing.

[e] 1981 expansion to 59 Gg/yr based on propylene oxidation to acrylic acid.

[f] High-pressure modified Reppe process for acrylic acid.

[g] Direct esterfication.

[h] Low-pressure modified Reppe process being phased out. Transesterification is used for higher esters.


NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
WISCONSIN
MICHIGAN
NEW YORK
IOWA
NEBRASKA
ILLINOIS
INDIANA
OHIO
PENNSYLVANIA
MISSOURI
KANSAS
KENTUCKY
NORTH CAROLINA
OKLAHOMA
TEXAS
ARKANSAS
TENNESSEE
SOUTH CAROLINA
MISSISSIPPI
ALABAMA
GEORGIA
LOUISIANA
FLORIDA
2
4
1
3
5

1. Celanese, Clear Lake, TX
2. Celanese, Pampa, TX
3. Dow Badische, Freeport, TX
4. Rohm and Haas, Deer Park, TX
5. Union Carbide, Taft, LA

Fig. II-1. Locations of Plants Manufacturing Acrylic Acid and Esters

and Haas low-pressure modified Reppe process plant, which produces the lower esters directly and the heavy esters by transesterification.

The overall annual growth for AA for the period between 1976 and 1982 is expected to be 8%; an annual growth for the propylene oxidation process for AA is assumed to be 15% and a -4% growth is assumed for the high-pressure modified Reppe process. Production of acrylic acid in 1974 and 1975 (including that used in ester manufacture) was 109 Gg and 95 Gg, respectively. Total ester production for these two years was 243 Gg and 209 Gg, respectively.[4]

C. REFERENCES*

1. R. W. Serth, D. R. Tierney, and T. W. Hughes, Source Assessment: Acrylic Acid Manufacture State-of-the-Art (on file at IERL, EPA, Cincinnati, OH).

2. Nonconfidential information received May 1978 from Celanese Chemical Co., Houston, TX (on file at EPA, ESED, Research Triangle Park, NC).

3. J. W. Blackburn, IT Enviroscience, Trip Report on Site Visit to Union Carbide Corp., South Charleston, WV, Dec. 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

4. J. L. Blackford, "CEH Marketing Research Report on Acrylic Acid and Esters," pp. 606.4031A-E, 606.4032A-Z, and 606.4033A-J in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (August 1976).

5. "Dow Badische Expands," Chemical Week 122(18), 17 (1978).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTIONS

A. ACRYLIC ACID PRODUCTION

1. Introduction

Three processes are currently used to manufacture AA. The first, propylene oxidation, represents 66% of the present U.S. capacity for AA. The remaining 34% represents the high- and low-pressure modified Reppe processes (181.6 Gg/yr of this modified Reppe process is catagorized as idle capacity and is being phased out with the addition of a new propylene oxidation plant of equal capacity). Not including the low pressure modified Reppe plant being phased out, 94% of U.S. AA capacity uses propylene oxidation technology, and 6% uses the high-pressure modified Reppe process.

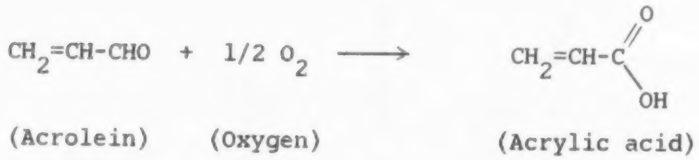
2. Propylene Oxidation Process

a. Basic Process -- AA is produced by the following chemical reactions:[1,2]

(1) $CH_2{=}CH{-}CH_3 + O_2 \longrightarrow CH_2{=}CH{-}CHO + H_2O$

(Propylene) (Oxygen) (Acrolein) (Water)

(2)



$$CH_2{=}CH{-}CHO + 1/2\ O_2 \longrightarrow CH_2{=}CH{-}C\overset{\displaystyle O}{\underset{\displaystyle OH}{\smash{\diagup}}}$$

The process flow diagram shown in Fig. III-1 represents a typical process using two-stage propylene oxidation for AA production. Single-stage oxidation is feasible but is not as economical as a two-stage process.[1]

Catalysts used in the oxidation of propylene to acrylic acid are the focus of considerable patent activity. They vary in composition and may include molybdenum, cobalt, iron, bismuth, tin, tungsten, tellurium, sodium, and other metallic elements. These proprietary mixtures are in the form of pellets or are fixed on inert supports.[2,3]

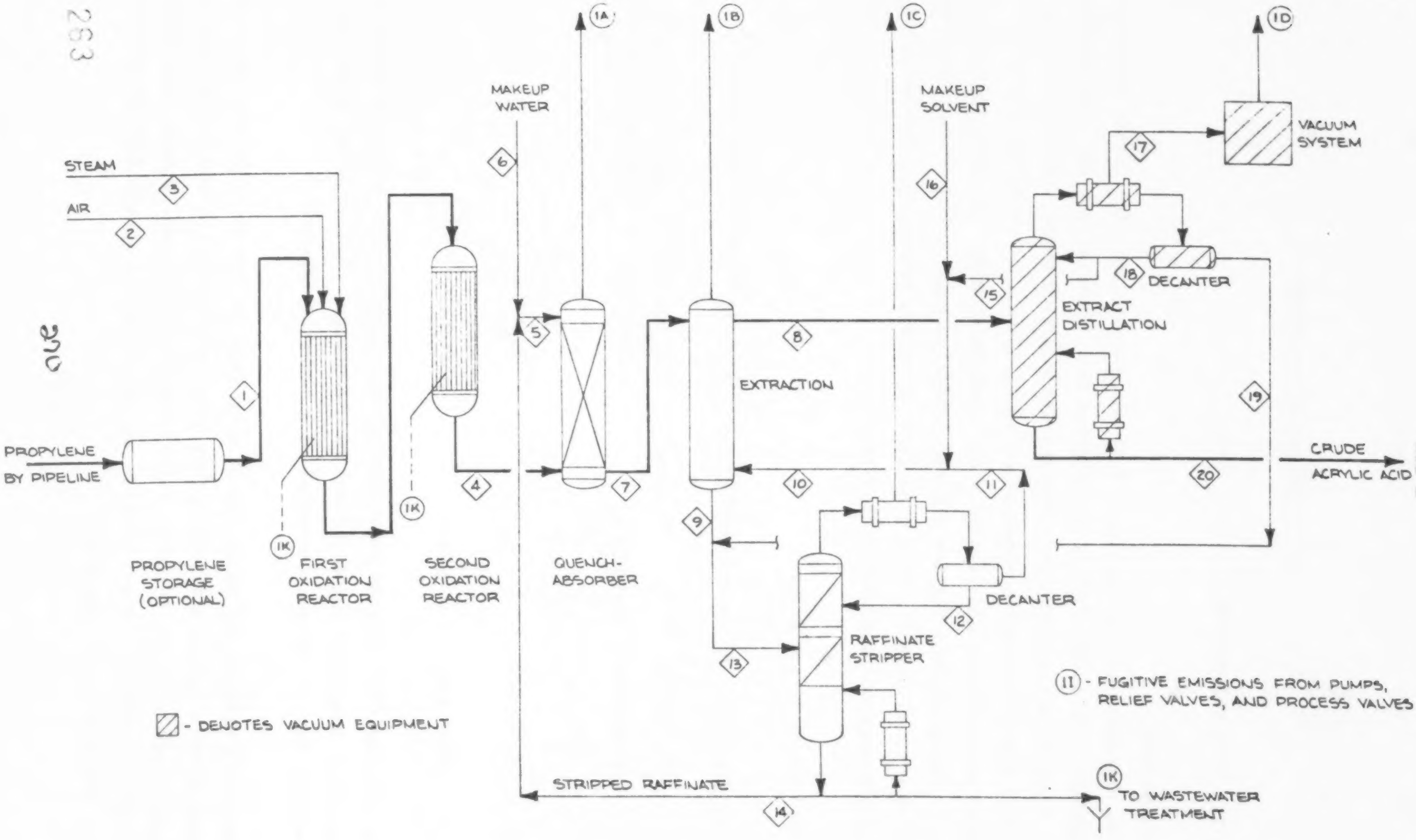

PROPYLENE BY PIPELINE
PROPYLENE STORAGE (OPTIONAL)
FIRST OXIDATION REACTOR
SECOND OXIDATION REACTOR
QUENCH-ABSORBER
EXTRACTION
RAFFINATE STRIPPER
DECANTER
EXTRACT DISTILLATION
DECANTER
VACUUM SYSTEM
STEAM
AIR
MAKEUP WATER
MAKEUP SOLVENT
CRUDE ACRYLIC ACID
STRIPPED RAFFINATE
TO WASTEWATER TREATMENT
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
1A
1B
1C
1D
1K
1K
1K
▨ - DENOTES VACUUM EQUIPMENT
(1I) - FUGITIVE EMISSIONS FROM PUMPS, RELIEF VALVES, AND PROCESS VALVES

Fig. III-1. Manufacture of Acrylic Acid from Propylene

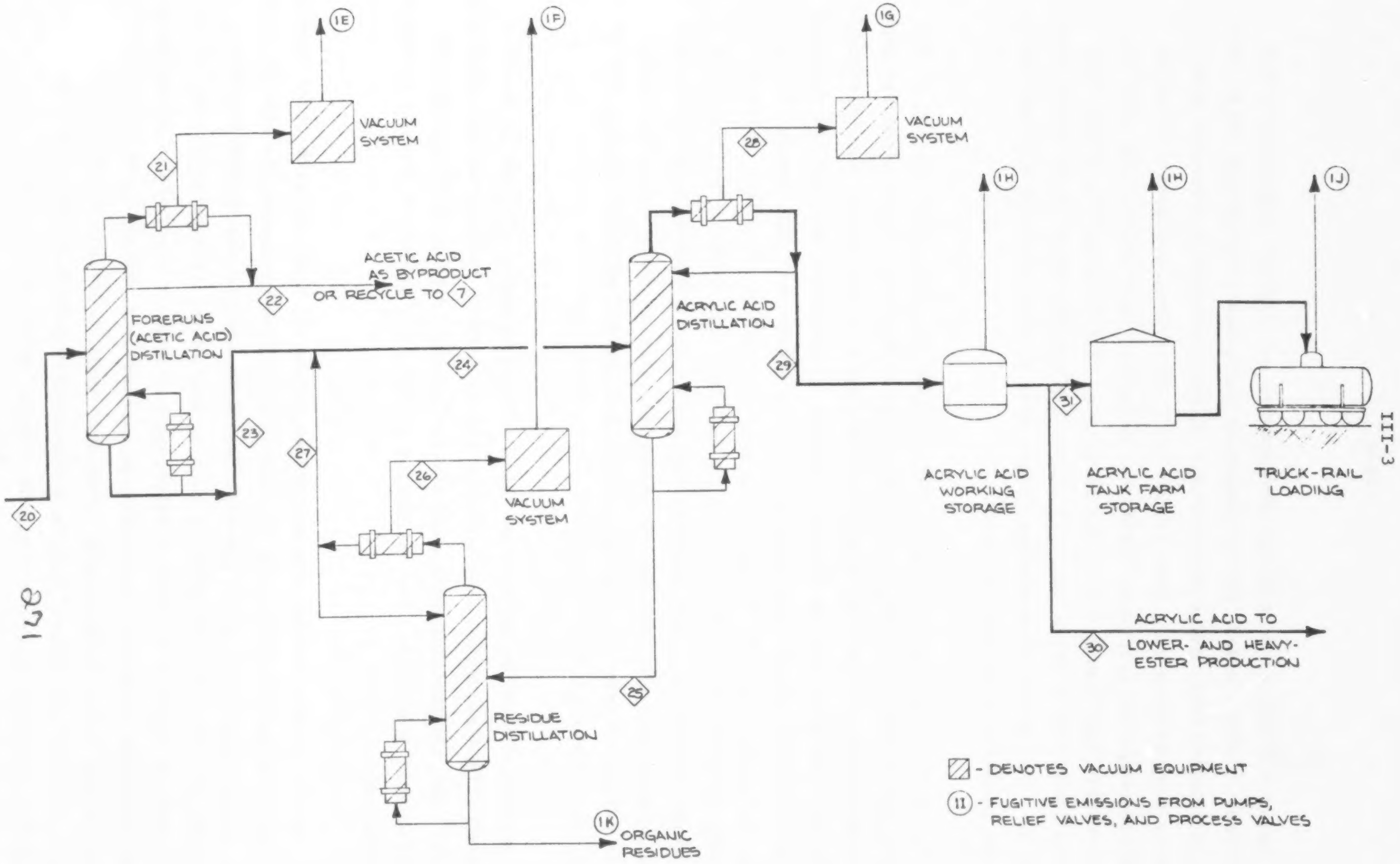

1E
VACUUM SYSTEM
21
1F
1G
28
VACUUM SYSTEM
ACETIC ACID AS BYPRODUCT OR RECYCLE TO 7
22
FORERUNS (ACETIC ACID) DISTILLATION
24
ACRYLIC ACID DISTILLATION
29
1H
1H
1J
23
27
26
VACUUM SYSTEM
20
31
ACRYLIC ACID WORKING STORAGE
ACRYLIC ACID TANK FARM STORAGE
TRUCK-RAIL LOADING
ACRYLIC ACID TO LOWER- AND HEAVY-ESTER PRODUCTION
30
25
RESIDUE DISTILLATION
1K
ORGANIC RESIDUES
▨ - DENOTES VACUUM EQUIPMENT
(11) - FUGITIVE EMISSIONS FROM PUMPS, RELIEF VALVES, AND PROCESS VALVES

Fig. III-1. (Continued)

The major differences in catalyst performance are reactor temperatures and pressures, contact times, air-to-propylene and steam-to-propylene molar feed ratios, conversions, and selectivities. Patent literature indicates that reactor temperatures vary from 130 to 480°C in systems designed for acrylic acid production by propylene oxidation; pressures vary from 5.1 to 1210 kPa; and contact times range from 0.001 to 46 sec. Air-to-propylene molar feed ratios range from 0.07 to 66.7 and steam-to-propylene molar feed ratios from 0 to 50. Conversion of propylene ranges from 12.1 to 100 mole %. Wide variations in selectivity are reported.[3]

In Fig. III-1 propylene (Stream 1), air (Stream 2), and steam (Stream 3) are fed to the oxidation reactors in proportions within the ranges discussed above. The steam helps control the reaction temperature, conversions, and selectivities. Since the reactions are exothermic, reactor heat-removal systems are required to maintain the appropriate temperatures and pressures. The gaseous effluent from the second reactor (Stream 4) is sent to a quench-absorber, where it is rapidly quenched with water (Stream 5) to remove the organic water-soluble compounds (Stream 7). The water stream fed to the quench-absorber includes some aqueous effluent (Stream 14) generated later in the process and fresh water makeup (Stream 6). The gas stream leaving the absorber (Stream 1A) is a major process emission.

The aqueous stream containing the water-soluble organics (Stream 7) is extracted with a solvent. Many solvents can be used to extract acrylic acid from water,[2] but the specific ones used are considered to be proprietary by most acrylic acid producers. The extraction column is a source of organic emissions (Stream 1B).

The aqueous stream leaving the extraction column is combined with other aqueous streams from decanters (Stream 19) and is distilled to remove the solvent from the water. Some of this stripped raffinate is sent to the quench-absorber (Stream 14), and the remainder is sent to wastewater treatment (Stream 1K). This aqueous waste will contain water-soluble organic by-products of the propylene oxidation reaction: acetaldehyde, acetic acid, maleic acid, phthalic acid, formic acid, formaldehyde, propionic acid, propionaldehyde, acetone, allyl alcohol, and others[2] and is a source of a secondary emission. The vent from the raffinate stripper contains organic emissions (Stream 1C).

The extract stream (Stream 8) is distilled under vacuum to recover the solvent from the crude acrylic acid (Stream 20). The solvents may carry water overhead, requiring a decanter to separate the solvent (Stream 18) phase from the aqueous (Stream 19). The solvent (Stream 18) not used as column reflux (Stream 15) is combined with fresh solvent (Stream 16) and solvent from the raffinate stripper (Stream 11) and recycled to the extraction column (Stream 10). The vapors drawn from the extract distillation equipment by vacuum equipment (Stream 17) are ducted to a condenser and recovered. Uncondensed vapors are emitted (Stream 1D). Nitrogen is bled into the vacuum distillation equipment to maintain the vacuum and avoid further oxidation of acrylic acid.[4]

Crude acrylic acid (Stream 20) is sent to another vacuum distillation system -- the foreruns distillation -- where compounds more volatile than acrylic acid are removed. The foreruns distillation effluent (Stream 22) is largely acetic acid and can be further purified to produce glacial acetic acid as a by- product. Most manufacturers return this stream to the extraction column feed (Stream 7), and the acetic acid ultimately leaves the system in the stripped raffinate wastewater. The vapors (Stream 21) drawn from the foreruns distillation are ducted to a condenser. Uncondensed vapors are emitted (Stream 1E).

The acrylic acid (Stream 23) is then combined with the acrylic acid from a residue distillation (Stream 27) and is fed (Stream 24) to a vacuum distillation unit, where acrylic acid is taken overhead (Stream 29). Vapors drawn from this equipment (Stream 28) are ducted to a condenser. Uncondensed vapors are emitted (Stream 1G).

Bottoms from the acrylic acid distillation (Stream 25) are distilled in residue distillation equipment, and the acrylic acid removed (Stream 27) is recycled to the acrylic acid distillation. Emissions from this vacuum equipment are shown as Stream 1F in Fig. III-1. The residues (Stream 1K) are either liquid or solid organic wastes for disposal or by-products to be used in other acrylic processes.

Acrylic acid (Stream 29) is stored in temporary storage or "working storage" and then either sent to lower- and heavy-ester production or prepared for shipment by barge, truck, rail, or drum. All working tanks are shown as a single tank on Fig. III-1. Storage emissions are labeled Stream 1H, and emissions relating to packaging or shipping acrylic acid are labeled 1J.

Because of buildup of solid polymerization products of acrylic acid and acrylates, acrylic acid plants must be shut down for cleaning and maintenance from four to twelve times a year.[4] These polymers have to be manually removed. Although care is taken to avoid their formation, as much as 8 m^3/yr or about 1200 kg/yr, of organic solids can be generated. The material is disposed of by incineration[4,5] or landfill.[6]

When equipment is shut down for cleaning, care is taken not to produce organic emissions. After the organics have been removed, nitrogen is introduced into the equipment to prevent entrance of air. Upon startup the equipment is filled with process fluids and/or placed under vacuum; the nitrogen displaced contains little organic.[4]

Fugitive losses (labeled 1I on Fig. III-1) can occur at valves and seals and may contain propylene, acrylic acid, acrolein, solvent, and other organics. Much of the process shown in Fig. III-1 is under vacuum, and so the tendency is for air to leak into the equipment rather than for organics to leak out of the equipment. However, situations can exist where, because of the static liquid head, the localized pressures generated can be greater than atmospheric. In these cases it is possible for fugitive leaks to occur from equipment maintained under vacuum.

Storage emission sources (labeled 1H on Fig. III-1) are related to acrylic acid and solvent storage. Both working and tank farm storages are shown.

Handling emissions (labeled 1J on Fig. III-1) arise from loading of acrylic acid into drums, tank trucks, tank cars, or barges.

b. Process Variations -- Manufacturers of acrylic acid use a number of variations of the process. Because the manufacture of acrylic acid is highly competitive and the propylene oxidation process is relatively new, many producers consider the specific details of the reaction catalysts, conditions, raw material ratios, etc., as confidential. This is also true of the design of the quench-absorber since knowledge of the details of flow, composition, and conditions of the entering and exiting streams can reveal details of the oxidation reactor. Operating conditions and stream compositions and flow can vary widely, as has been shown.

The step of extraction of acrylic acid from the aqueous quench-absorber effluent also varies widely. Many different solvents -- with different molecular weights, vapor pressures, aqueous solubilities, and distribution coefficients --may be used.[2] This is also a sensitive area from the manufacturer's viewpoint. The ratio of solvent to feed varies with the solvent used, and the extract distillation equipment must be designed with consideration of this ratio and other factors, such as the physical properties of the chemicals. The raffinate stripper design depends on the volume of water in the system (which in turn depends on the amount of steam fed, the amount of water produced in the reaction, and the amount of makeup water added) and on the aqueous solubility of the solvent selected for use.

The design of the foreruns distillation depends on whether the manufacturer intends to recover acetic acid (a major impurity) or to waste the foreruns in the stripped raffinate. In a plant producing acetic acid additional equipment may be used to purify the acetic acid or to remove other specific impurities from the acrylic acid.

The acrylic acid distillation may consist of several pieces of distillation equipment, generating acrylic acid of various purities. Residue distillation is designed for the type and efficiency of polymerization inhibitor used[2] and the amounts of other impurities of low volatility.

In general the distillation equipment following the extraction may be highly individualized in design. Although several stills may be used, only one is shown in Fig. III-1.

Storage practices for acrylic acid depend on whether all acrylic acid is used captively for ester production at a plant or whether some acrylic acid is sold to outside consumers or transferred to different plant locations. Acrylic acid storage requires special precautions to prevent further acrylic acid oxidation or polymerization. A variety of residual inhibitors and nitrogen blankets may be used to minimize oxidation or polymerization of acrylic acid being stored.[1,4] Freezing of the acrylic acid in storage must also be avoided since freezing may cause the inhibitors to separate from the bulk of the acrylic acid.

3. Modified Reppe Processes

Rohm and Haas currently uses the low-pressure modified Reppe process,[7] only to meet peak product demand. This process does not produce acrylic acid since it makes the lower esters directly. Rohm and Haas (Deer Park, TX) is phasing out production of lower esters by this route and has recently (1977) introduced a new propylene oxidation process.

The Dow Badische plant uses the high-pressure modified Reppe process and has a capacity of 6% of total domestic acrylate (excluding the old Rohm and Haas low-pressure modified Reppe process).

The high-pressure modified Reppe process is significantly different from the low-pressure process. Since the high-pressure process is used for only a small percentage of today's acrylate capacity and since it is expected to be phased out when a proposed propylene oxidation plant is built in 1981,[8] those interested in it are referred to the literature.[9]

4. Other Processes

Acrylic acid can also be produced by hydrolysis of acrylonitrile. This process is unattractive because of higher capital costs and the generation of large amounts of sulfuric acid--ammonium sulfate wastes. Acrylic acid can be produced by pyrolysis of acetic acid or acetone to ketene, and then conversion of the ketene to β-propiolactone. Because β-propiolactone is a suspected carcinogen, this reaction is not recommended. Acrylic acid can also be manufactured from ethylene cyanohydrin. Although this was the first process commercially used for acrylic acid production, yields are low and larger amounts of sulfuric acid--ammonium sulfate wastes are generated.

Although there are other possible processes[1] for acrylic acid manufacture, none are currently used in the U.S.[1,10]

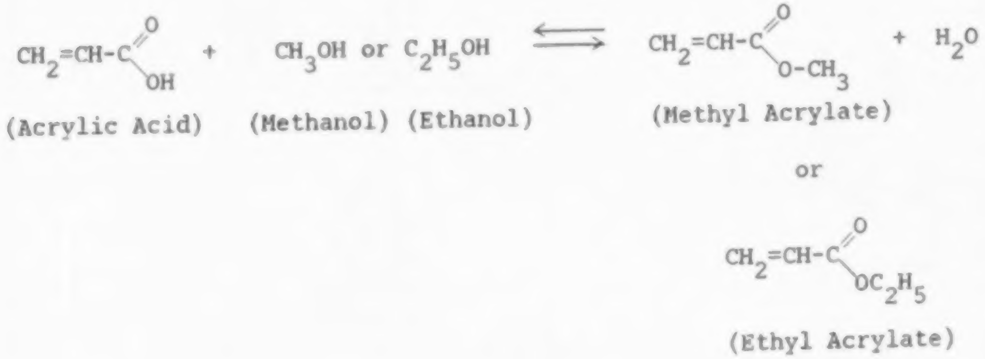
B. LOWER-ACRYLIC-ESTER PRODUCTION

1. Introduction

Lower esters -- methyl and ethyl acrylate -- are normally produced by direct esterification of acrylic acid with methanol or ethanol or by other, undisclosed, processes. Low-pressure modified Reppe plants produce the lower acrylates without isolating acrylic acid.[1]

2. Direct Esterification

a. Basic Process -- Methyl and ethyl acrylates are produced from acrylic acid and methanol or ethanol by the reaction



$$CH_2{=}CH{-}C(=O)OH + CH_3OH \text{ or } C_2H_5OH \rightleftarrows CH_2{=}CH{-}C(=O){-}O{-}CH_3 + H_2O$$

(Acrylic Acid) (Methanol) (Ethanol) (Methyl Acrylate)

or

$$CH_2{=}CH{-}C(=O)OC_2H_5$$

(Ethyl Acrylate)

This reaction involves an equilibrium relationship; a strong acid, such as sulfuric, is often used to catalyze the forward reaction.[1,11]

The process flow diagram shown in Fig. III-2 represents a typical process using direct esterification to manufacture lower esters. Acrylic acid (Stream 1), methyl or ethyl alcohol (Stream 2), and sulfuric acid (Stream 3) are fed to an esterification reactor equipped for reflux distillation. Vapors leaving the reflux distillation are condensed and form a two-phase mixture (Stream 5 and 6) of acrylate ester, water, alcohol, and traces of acrylic acid. Organic emissions can occur (Stream 3A). The aqueous layer (Stream 6) is combined with other aqueous streams and sent to an alcohol recovery distillation (Stream 11). Noncondensables from this equipment are organic emissions (Stream 3B). Bottoms from the esterification reactor (Stream 8) are distilled in a bottoms stripper

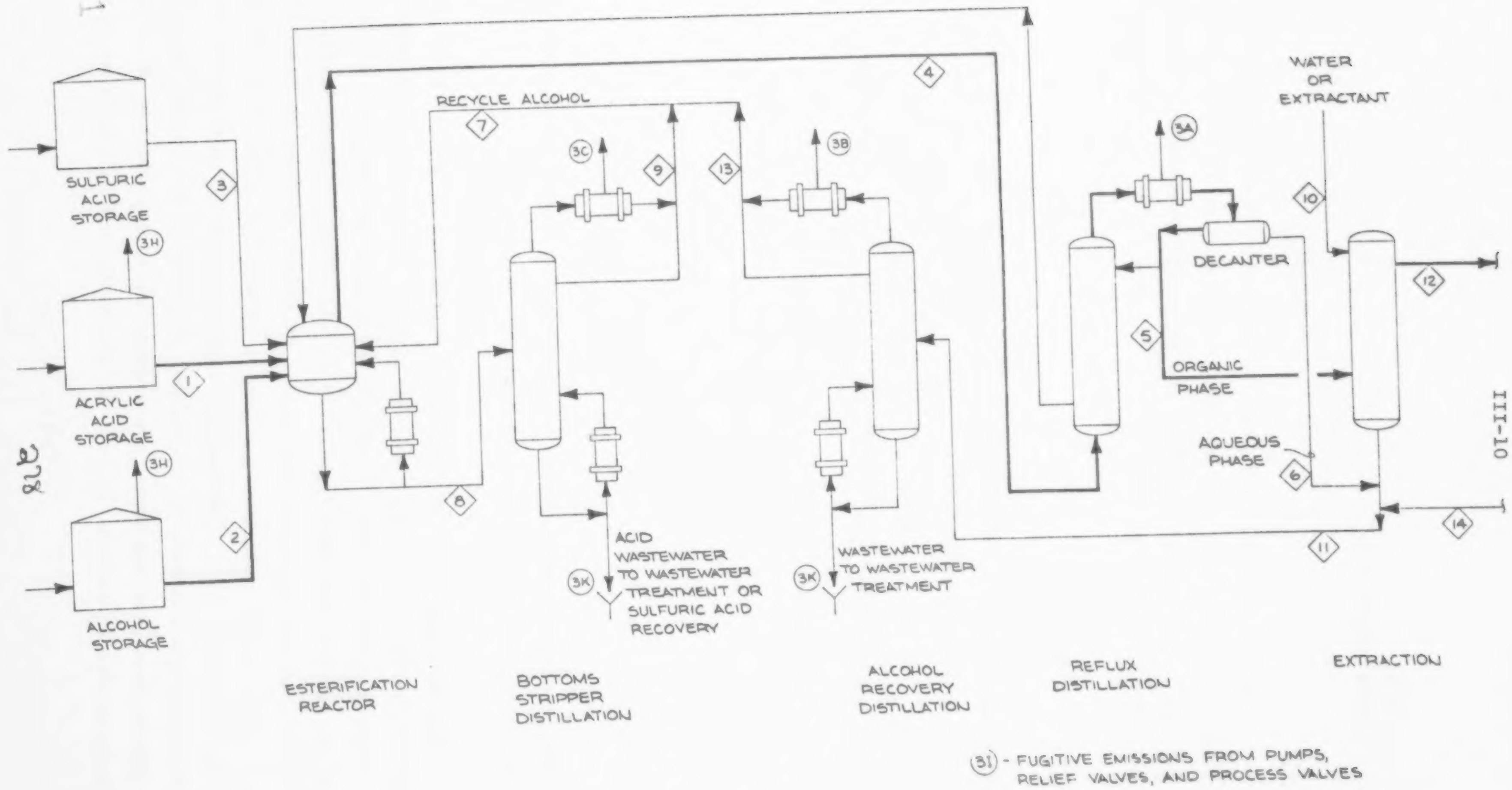

SULFURIC ACID STORAGE
ACRYLIC ACID STORAGE
ALCOHOL STORAGE
3H
3H
1
2
3
RECYCLE ALCOHOL
4
5
6
7
8
9
10
11
12
13
14
3A
3B
3C
3K
3K
ACID WASTEWATER TO WASTEWATER TREATMENT OR SULFURIC ACID RECOVERY
WASTEWATER TO WASTEWATER TREATMENT
DECANTER
ORGANIC PHASE
AQUEOUS PHASE
WATER OR EXTRACTANT
ESTERIFICATION REACTOR
BOTTOMS STRIPPER DISTILLATION
ALCOHOL RECOVERY DISTILLATION
REFLUX DISTILLATION
EXTRACTION
(3I) - FUGITIVE EMISSIONS FROM PUMPS, RELIEF VALVES, AND PROCESS VALVES

Fig. III-2. Manufacture of Lower Acrylic Acid Esters by Direct Esterification

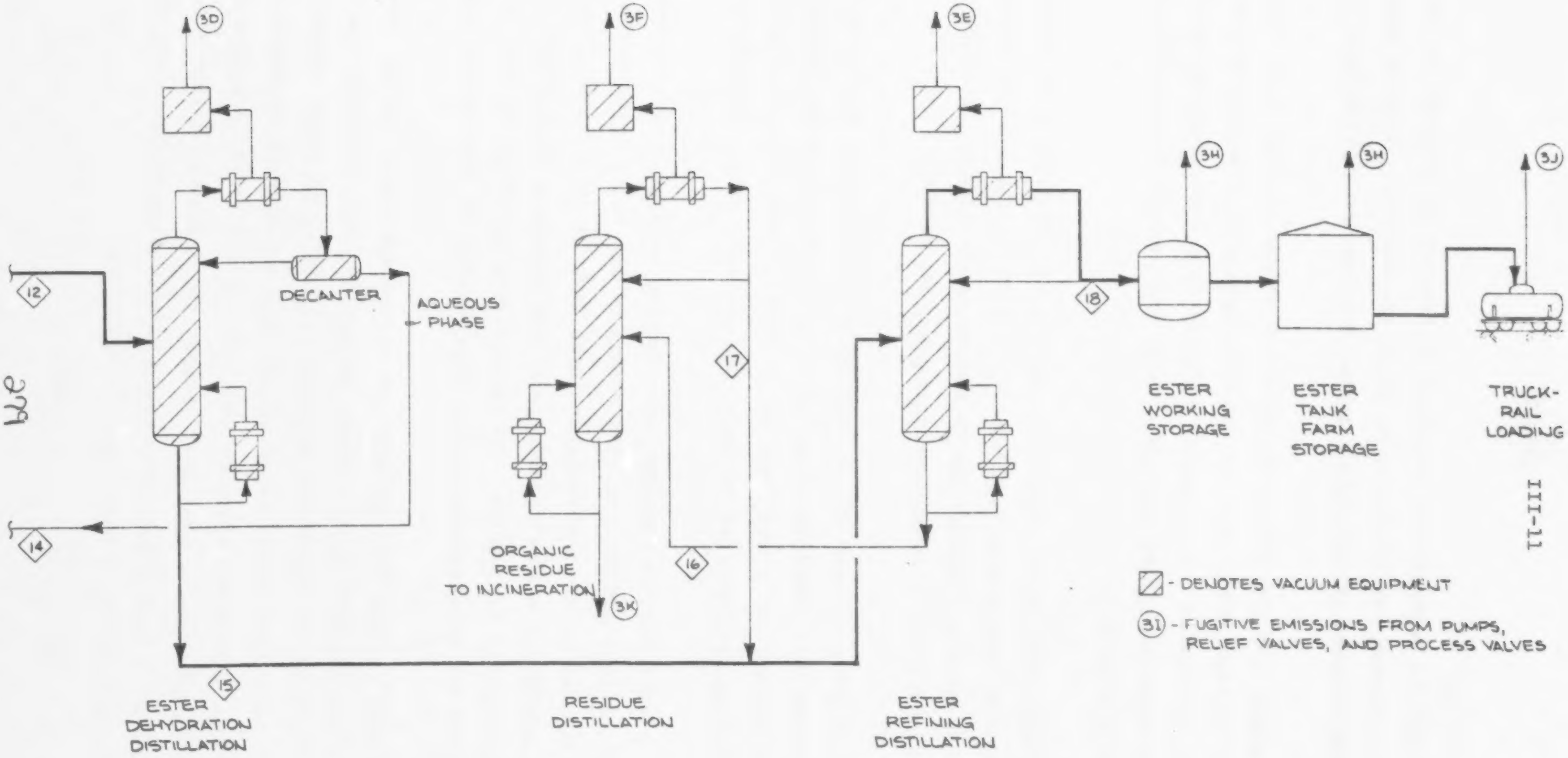

3D
3F
3E
3H
3H
3J
12
DECANTER
AQUEOUS PHASE
17
18
ESTER WORKING STORAGE
ESTER TANK FARM STORAGE
TRUCK-RAIL LOADING
14
ORGANIC RESIDUE TO INCINERATION
3K
16
15
ESTER DEHYDRATION DISTILLATION
RESIDUE DISTILLATION
ESTER REFINING DISTILLATION
▨ - DENOTES VACUUM EQUIPMENT
③I - FUGITIVE EMISSIONS FROM PUMPS, RELIEF VALVES, AND PROCESS VALVES

Fig. III-2. (Continued)

distillation and the organic-rich overhead (Stream 9) is returned to the reactor with other alcohol-containing distillates (Stream 13). Organic emissions from uncondensed vapors in this distillation are labeled (Stream 3C).

The organic phase from the reflux distillation column (Stream 5) is extracted with water or another extractant (Stream 10) capable of removing the alcohol from the feed (Stream 5). The aqueous effluent from the extractor is combined with other alcohol-containing aqueous streams and sent to the alcohol recovery distillation (Stream 11).

The organic phase leaving the extractor (Stream 12) is sent to an ester dehydration distillation, where dissolved water is removed. The aqueous phase from the associated decanter (Stream 14) is routed to the alcohol recovery distillation along with other alcohol-containing aqueous streams.

The dehydrated ester (Stream 15) is refined by distillation and stored for shipping (Stream 18). Residues from the refining distillation (Stream 16) are distilled to recover ester and then incinerated (Stream 3K). Overheads from this distillation are returned to the ester-refining column (Stream 17).

Lower-ester plants require shutdown and cleaning because of the tendency of the esters to polymerize and because of a change of the ester being produced. This has been estimated by one manufacturer to be from 12 to 24 times a year. Nitrogen blankets are used to prevent air from entering the equipment, and organics are removed as liquids. In these plants shutdown is usually performed in preparation for idle standby rather than because of operational problems.[4]

Fugitive losses (Stream 3I) can occur at valves and seals and may consist of methyl or ethyl alcohol, acrylic acid, methyl or ethyl acrylate, and other organics. Some of the equipment shown in Fig. III-2 is under vacuum and should, in general, have fewer fugitive emissions than atmospheric equipment. It is still possible that some emissions can occur if the static pressure at any point exceeds atmospheric pressure. Pumps, for instance, either receiving or pumping against a high liquid head could be operating at pressures greater than atmospheric and therefore have fugitive emissions.

Storage emission sources (Stream 3H) are acrylic acid, methyl and/or ethyl alcohol, and product methyl acrylate and/or ethyl acrylate working and tank farm storage units. Sulfuric acid storage and water storage will create no organic emissions. If the extractant (Stream 10) for the organic phase from the reflux distillation column is organic, it will require storage and will result in an organic emission.

Handling emissions (Stream 3J) will occur from loading the acrylate esters in drums, tank cars, tank trucks, and barges.

b. Process Variations -- Other acid catalysts, e.g., sulfonic acids and strong-acid ion exchange resins, may be used for direct esterification.[1] Manufacturers have the option of recovering any of the acid catalysts or disposing of them by neutralization and waste treatment. Since ion exchange resins are expensive, ion exchange systems will require resin regeneration equipment.

Some manufacturers may use vacuum equipment for distillations instead of the atmospheric equipment shown on Fig. III-2. In general the organic emissions generated by vacuum distillations are expected to exceed those generated by atmospheric pressure equipment, since vacuum distillations will have air leaks in addition to the nitrogen bled into the system. These inert gases will pass through the condensers as noncondensable gases.

Extractants other than water may be used to remove the alcohols from the overheads of the reflux distillations. Specific data are considered to be confidential by the manufacturers.

3. Production of Butyl Acrylates by Direct Esterification

Flow diagrams for producing butyl acrylate esters are similar to those of Fig. III-2. However, butanol must be removed from the butyl acrylate stream (Stream 15) by azeotropic distillation. The butanol--butyl acrylate azeotrope would be returned to the esterification reactor.[1] The equipment is probably not vacuum equipment.

C. HEAVY-ESTER PRODUCTION

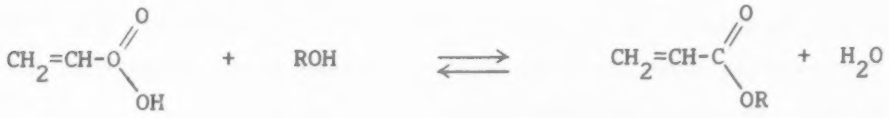
1. Introduction

Heavy esters such as 2-ethylhexyl acrylate may be produced by direct esterification of acrylic acid with a heavy alcohol. This is the preferred method,[1] although plants that isolate acrylic acid may also use transesterification of a lower ester and a heavy alcohol to a heavy ester and a lower alcohol. Plants that produce the lower esters directly must use transesterification. With the replacement by Rohm and Haas of the low-pressure modified Reppe process by the propylene oxidation process, transesterification will also be phased down.

Heavy-ester plants are normally smaller, batch production plants as opposed to the larger, continuous lower-ester plants because the lower demand for the heavy esters necessitates higher production flexibility.[1]

2. Direct Esterification

a. Basic Process -- Heavy acrylates are produced by direct esterification according to the reaction



(Acrylic acid) (Heavy Alcohol) (Heavy Ester) (Water)

The process flow diagram shown in Fig. III-3 represents a typical process using direct esterification for heavy ester manufacture. The acrylic acid (Stream 1), the heavy alcohol (Stream 2), the acid catalyst (Stream 3), and a solvent (Stream 4) are added to an esterification reactor-distillation, where the reaction then proceeds. The water of reaction is removed by an entraining solvent,[1] and the vapors are condensed (Stream 5) and decanted. The solvent phase is returned to the reactor-distillation, and the aqueous phase is sent to waste disposal (Stream 5K). Organic emission from the esterification reactor-distillation is labeled 5A on Fig. III-3.

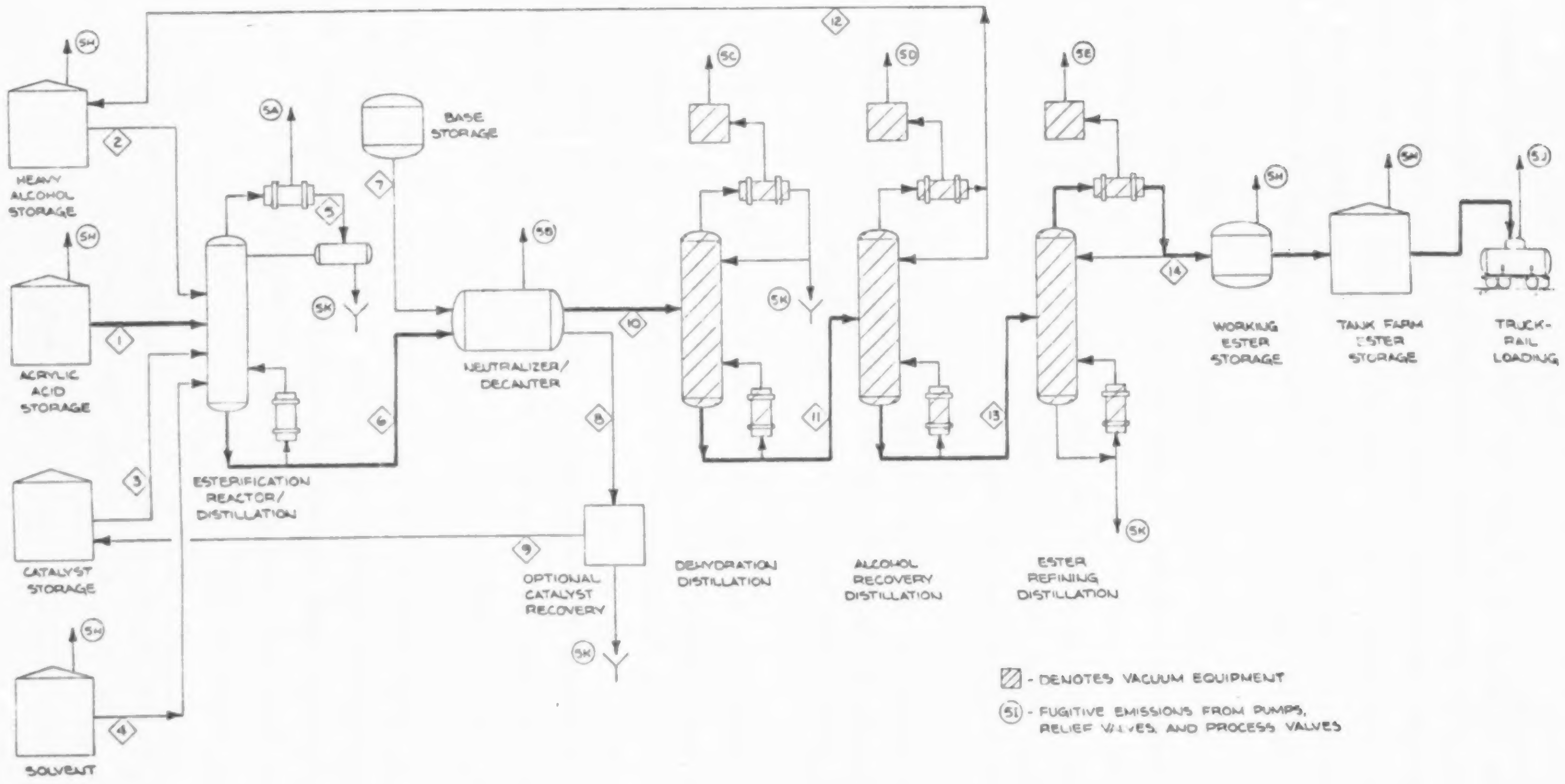

HEAVY ALCOHOL STORAGE
ACRYLIC ACID STORAGE
CATALYST STORAGE
SOLVENT
5H
5H
5H
1
2
3
4
5
6
7
8
9
10
11
12
13
14
5A
5B
5C
5D
5E
5K
5K
5K
5K
5H
5M
5J
BASE STORAGE
ESTERIFICATION REACTOR/ DISTILLATION
NEUTRALIZER/ DECANTER
OPTIONAL CATALYST RECOVERY
DEHYDRATION DISTILLATION
ALCOHOL RECOVERY DISTILLATION
ESTER REFINING DISTILLATION
WORKING ESTER STORAGE
TANK FARM ESTER STORAGE
TRUCK-RAIL LOADING
▨ - DENOTES VACUUM EQUIPMENT
(5I) - FUGITIVE EMISSIONS FROM PUMPS, RELIEF VALVES AND PROCESS VALVES

Fig. III-3. Manufacture of Heavy Acrylic Acid Esters by Direct Esterification

The bottoms from the esterification reactor-distillation contain the heavy ester, unreacted heavy alcohol, unreacted acrylic acid, acid catalyst, and other materials (Stream 6). This stream is neutralized with a base, and the phases are separated. The aqueous phase (Stream 8) may be processed to recover the acid catalyst (Stream 9) or sent to waste treatment (Stream 5K). Organic emissions from the neutralizer-decanter are labeled 5B on Fig. III-3.

The organic phase (Stream 10) is dehydrated in a vacuum dehydration distillation. The water removed (Stream 5K) is sent to waste treatment. Unreacted heavy alcohol is recovered in a vacuum alcohol recovery distillation (Stream 12) and returned to storage. The crude heavy ester (Stream 13) is then refined in a vacuum ester refining distillation and the refined heavy ester is stored for shipping (Stream 14).

The batch nature of the heavy-ester plants requires shutdown and cleaning at the conclusion of each heavy-ester run. The shutdown frequency depends on how often the heavy ester being produced is changed.

Fugitive losses (5I on Fig. III-3) can occur from valves and seals. These emissions can contain heavy alcohols, acrylic acid, acid catalyst (if organic), heavy ester, and entraining solvent. Some of the equipment shown in Fig. III-3 is under vacuum. As was discussed earlier, vacuum equipment should have fewer fugitive emissions than atmospheric equipment. It is still possible that some emissions can occur if the static pressure at any point exceeds atmospheric pressure, e.g., at pumps either receiving or pumping against a high liquid leg.

Storage emission sources (5H on Fig. III-3) are related to acrylic acid storage, heavy-alcohol storage, and catalyst storage (if organic), entraining solvent storage, base storage (if organic), and heavy-ester storage. No organic emissions from acid catalyst storage or base storage will occur if these are inorganic acids and bases.

Handling emissions (5J on Fig. III-3) will occur from loading the heavy ester in drums, tank cars, tank trucks, and barges.

c. Process Variations -- The process used for heavy-ester production by direct esterification varies according to the the specific acid catalyst, entraining solvent, and base used. Certain acid catalysts (sulfonic acids, ion exchange resins) may require additional equipment for recovery or regeneration. Different entraining solvents have varying aqueous solubilities, resulting in different compositions of the solvents in the esterification reactor wastewater. If the solubility is high, additional distillation equipment may be used on this aqueous stream to strip the wastewater and recover the soluble solvent.

3. Heavy-Ester Production by Transesterification

a. Basic Process -- Heavy esters are produced by transesterification of lower esters according to the reaction[1]

$$CH_2{=}CHO_2R + R'OH \rightleftarrows CH_2{=}CHCO_2R' + ROH$$

where ROH is the lower alcohol and R'OH is the heavy alcohol.

The process flow diagram for transesterification is similar to that shown in Fig. III-3 with the following exceptions: (1) the lower ester is stored instead of acrylic acid, (2) no entraining solvent is used, (3) the distillate from the esterification reactor-distillation (Stream 5) is an azeotrope of the lower alcohol and the heavy-ester product, (4) no neutralization is required, and (5) no dehydration distillation is required. The product from the esterification reactor-distillation is refined in an alcohol recovery distillation and ester refining distillation as shown.

Except for possible vacuum equipment discharges, no aqueous streams are generated in this process. Residues from the ester refining distillation and esterification reactor-distillation are incinerated.

Fugitive, storage, and handling emissions are similar to these described in the direct process.

D. REFERENCES*

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3. D. C. Thomas, "Acrylic Acid and Acrylic Esters, Supplement B, Process Economics Program, Stanford Research Institute, Menlo Park, CA (1974).

4. J. W. Blackburn, IT Enviroscience, Trip Report on Site Visit to Union Carbide Corp., South Charleston, WV, Dec. 8, 1977 (on file at the EPA, ESED, Research Triangle Park, NC).

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11. R. T. Morrison and R. N. Boyd, Organic Chemistry, p. 590, 2d ed., Allyn and Bacon, Boston, 1969.

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*Usually, when a reference number is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. INTEGRATED MODEL PLANT

With the exception of the Celanese Chemical Co. at Pampa, TX, all domestic manufacturers of acrylates produce acrylic acid and its esters at the same production site. Celanese at Pampa esterifies acrylic acid produced at its Clear Lake, TX, plant and shipped to Pampa. Producers of heavy esters purchase acrylic acid and perform esterification at other sites, but the amount of acrylates thus produced are small and are not considered in this report.

The model plant* used in the studies is based on an integrated acrylates facility producing acrylic acid by propylene oxidation and ethyl, butyl, and 2-ethylhexyl acrylates (EA, BA, 2-EHA) by direct esterification. The model plant has a total acrylate production capacity of 76.59 Gg/yr, broken down as follows:

Product	Capacity (Gg/yr)	Acrylic Acid Equivalent (Gg/yr)
AA	10	10
EA	38.94	33
BA	21.14	14
2-EHA	6.51	3
Total	76.59	60

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*See p. I-2 for a discussion of model plants.

This breakdown is based on actual acrylic acid consumption patterns for 1974 and 1975.[1] Reaction yields are assumed to be 70 mole % based on propylene going to acrylic acid and 85 mole % based on acrylic acid going to the esters.[2,3]

Methyl acrylate capacity is included with ethyl acrylate capacity. The amount of methyl acrylate produced is expected to be significantly smaller than the amount of ethyl acrylate. Emissions of the methyl ester may be slightly higher than those of the ethyl acrylate because of the higher volatility of methanol and methyl acrylate when compared with ethanol and ethyl acrylate.

Figure IV-1 shows the configuration of the model plant. The propylene oxidation step produces 60 Gg/yr of acrylic acid, one-sixth of which is sold as acrylic acid. The remaining five-sixths is reacted to form EA, BA, and 2-EHA in the proportions shown above. The model plant is operated 8760 hr/yr.* Atmospheric dispersion parameters for the model plant are given in Appendix B.

1. AA Unit of the Model Plant

The AA plant produces 60 Gg/yr of acrylic acid but does not produce acrolein or acetic acid for sale. Propylene enters the plant by pipeline and is stored only in temporary storage. These storage vessels have no emissions since they are pressure vessels and store a liquefied gas. A hypothetical solvent used to extract acrylic acid has a molecular weight of 60 and a vapor pressure of 34.5 kPa at storage conditions. These data are based on statistical analysis of highly volatile organic compounds stored in the United States and represent a statistical mean value for highly volatile solvents.[4] Tank farm storage for the AA-hypothetical solvent is 250 days, whereas process solvent storage is 7 days. Ten process-related tanks are shown as a single working tank on Fig. IV-1, each of which is sized for 5 days of storage. Acrylic acid is stored at the tank farm in four tanks, each sized for 20 days of storage. Table IV-1 summarizes storage tank data. Working and tank farm storage is based on data received from acrylic acid and ester manufacturers.[5,6]

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*Process downtime is normally expected to range from 5 to 15%. If the hourly production rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will normally operate on the same cycle as the process. Therefore, from the standpoint of cost effectiveness calculations, the error introduced by assuming continuous operation is negligible.

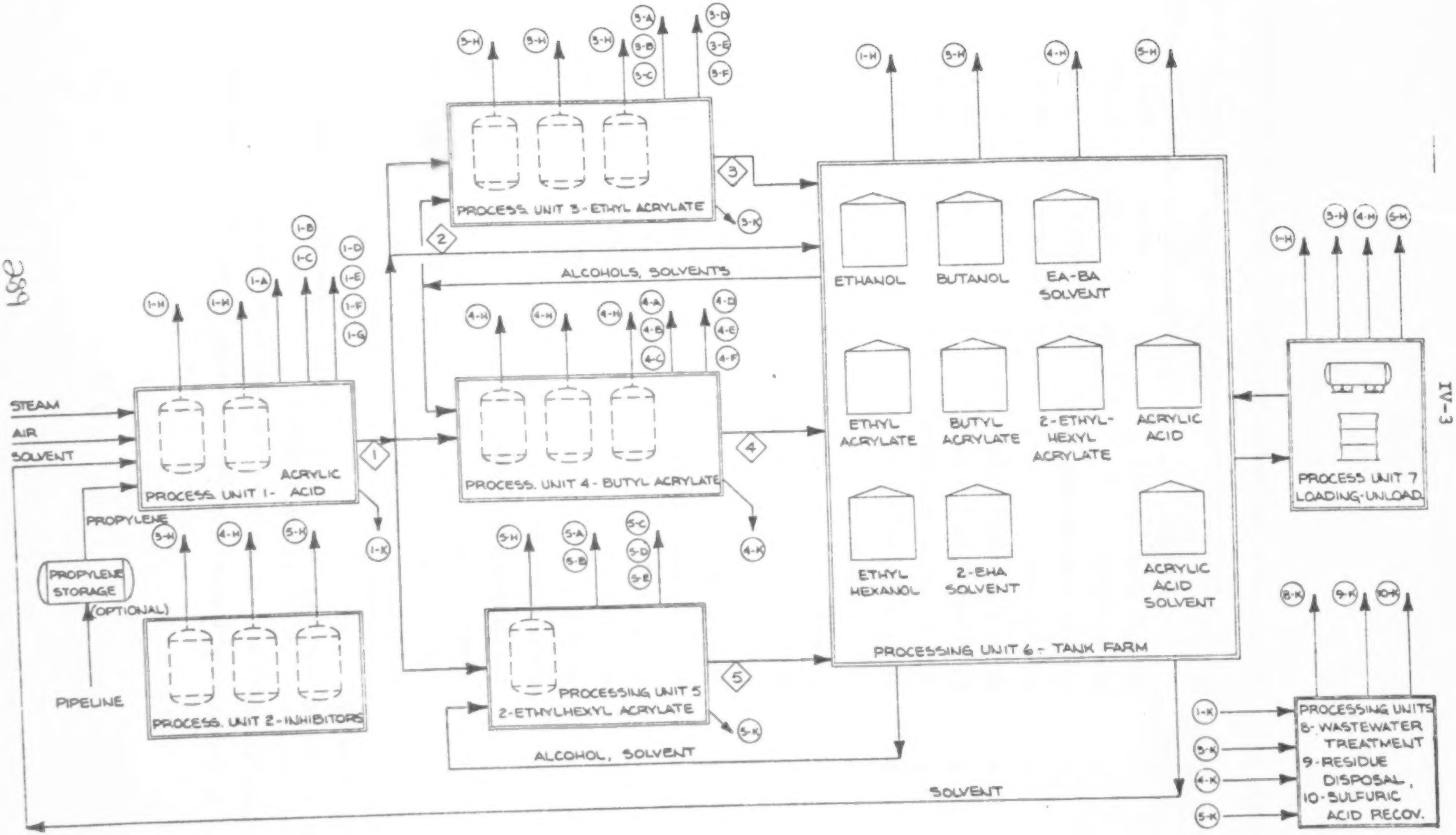
STEAM
AIR
SOLVENT
PROPYLENE
PROPYLENE STORAGE
(OPTIONAL)
PIPELINE
PROCESS UNIT 1- ACRYLIC ACID
1-H
1-H
1-A
1-B
1-C
1-D
1-E
1-F
1-G
1-K
1
PROCESS. UNIT 2-INHIBITORS
3-H
4-H
5-K
PROCESS. UNIT 3-ETHYL ACRYLATE
3-H
3-H
3-H
3-A
3-B
3-C
3-D
3-E
3-F
3-K
2
3
ALCOHOLS, SOLVENTS
PROCESS. UNIT 4-BUTYL ACRYLATE
4-H
4-H
4-H
4-A
4-B
4-C
4-D
4-E
4-F
4-K
4
PROCESSING UNIT 5 2-ETHYLHEXYL ACRYLATE
5-H
5-A
5-B
5-C
5-D
5-E
5-K
5
ALCOHOL, SOLVENT
SOLVENT
PROCESSING UNIT 6 - TANK FARM
1-H
3-H
4-H
5-H
ETHANOL
BUTANOL
EA-BA SOLVENT
ETHYL ACRYLATE
BUTYL ACRYLATE
2-ETHYL-HEXYL ACRYLATE
ACRYLIC ACID
ETHYL HEXANOL
2-EHA SOLVENT
ACRYLIC ACID SOLVENT
PROCESS UNIT 7 LOADING-UNLOAD
1-H
3-H
4-H
5-H
PROCESSING UNITS 8-WASTEWATER TREATMENT 9-RESIDUE DISPOSAL, 10-SULFURIC ACID RECOV.
1-K
3-K
4-K
5-K
8-K
9-K
10-K

Fig. IV-1. Model Plant for Manufacture of Acrylic Acid and Acrylic Acid Esters by Propylene Oxide

Table IV-1. Acrylic Acid and Esters Model-Plant Storage Requirements[a]

Process[b]	Type of Storage[c]	Content	Number of Tanks	Volume (m^3)	Turnovers per Year	Bulk Liquid Temperature(°
1	W	Acrylic acid solvent	1	90.58	52.1	20.3
1	W	Acrylic acid	10	0.333	73.0	27
1	T	Acrylic acid solvent	1	981.8	1.46	20.3
1	T	Acrylic acid	4	128.9	18.3	27
2 (3)[d]	W	Ethyl acrylate inhibitor	4	8.36	122	18.7
2 (4)	W	Butyl acrylate inhibitor	4	4.16	122	27
2 (5)	W	2-EH acrylate inhibitor	4	0.742	73.0	27
3	W	Ethyl acrylate solvent	2	27.73	365	20.3
3	W	Ethyl acrylate	4	55.45	122	18.7
3	W	Ethanol	1	55.45	365	27
3,4	T	EA-BA solvent	1	8521.0	6.08	20.3
3	T	Ethanol	1	4396.0	6.08	20.3
3	T	Ethyl acrylate	1	6941.0	6.08	21.4
4	W	Butyl acrylate solvent	1	26.22	365	20.3
4	W	Butyl acrylate	10	40.09	243	27
4	W	Butanol	1	48.45	365	27
4	T	Butanol	1	2921.0	6.08	20.3
4	T	Butyl acrylate	1	3870.0	6.08	28.1
5	W	2-ethylhexyl acrylate	8	5.71	209	32.6
5	T	2-EHA solvent	1	5.37	6.08	20.3
5	T	2-ethylhexanol	1	1603.0	4.06	20.3
5	T	2-ethylhexyl acrylate	3	403.7	6.08	29.8

[a] See refs. 5 and 6.

[b] Process defined as follows: 1 = acrylic acid; 2 = inhibitor makeup; 3 = ethyl acrylate; 4 = butyl acrylate; 5 = 2-ethylhexyl acrylate.

[c] W = process-related - working storage; T = tank farm storage.

[d] Numbers in parentheses indicate process to which emissions are prorated.

The number of valves and pumps is discussed in Sect. IV.B. The number of fugitive emission sources is based on data received from acrylic acid and ester manufacturers.[5]

2. EA Unit of the Model Plant

The EA model plant is based on the flowsheet in Fig. III-2 and produces 38.94 Gg/yr of ethyl acrylate. Sulfuric acid is used for the acid catalyst, and conventional sulfuric acid recovery is assumed. Vacuum equipment is as shown in Fig. III-2. A hypothetical solvent is used to extract ethyl acrylate from the reflux distillation overheads. This solvent also has a molecular weight of 60 and a vapor pressure of 34.5 kPa at storage conditions, but is not necessarily the same solvent as that used for acrylic acid.

Solvent for ethyl acrylate production is stored for 60 days at the tank farm and in two working tanks, each having 1 day of storage capacity. Ethanol is stored in a single tank for 60 days at the tank farm and in a single working tank having 1 day of storage. Ethyl acrylate is stored at the tank farm in one tank with 60 days of storage capacity and in four working tanks, each with 3 days of storage capacity. These data are based on data received from acrylic acid and ester manufacturers.[5,6] Ethyl acrylate storage requirements are summarized in Table IV-1.

The number of valves and pumps is discussed in Sect. IV.B. The number of fugitive emission sources is based on data received from acrylic acid and ester manufacturers.[5]

3. BA Unit of the Model Plant

The butyl ester model plant is based on the flowsheet in Fig. III-2 with the variations discussed in Sect. III.B.3.

The solvent used for butyl acrylate manufacture is a hypothetical solvent having a molecular weight of 60 and a vapor pressure of 34.5 kPa at storage conditions. This solvent is not necessarily the same as that used in acrylic acid manufacture but is assumed to be the same as the one used in ethyl acrylate manufacture. Therefore tank farm storage will be shared with that specified for ethyl acrylate. Solvent working storage is a single tank with 1 day of storage capacity.

n-Butanol is stored at the tank farm in a single tank having 60 days of storage capacity. One working tank stores n-butanol and has 1 day storage capacity. Butyl acrylate is stored at the tank farm in a single tank having 60 days of storage capacity. For working butyl acrylate storage there are ten tanks, each having 1.5 days of storage capacity. The storage requirements summarized in Table IV-1 are based on data supplied by acrylic acid and ester producers.[5]

The number of valves and pumps is discussed in Sect. IV.B. The number of fugitive emission sources is based on data received from acrylic acid and ester manufacturers.[5]

4. 2-EHA Unit of the Model Plant

The 2-EHA model plant is based on the flowsheet in Fig. III-3. The system assumes a sulfuric acid catalyst with sulfuric acid recovery. A hypothetical solvent to remove water of esterification is used. This solvent has a molecular weight of 60 and a vapor pressure at storage conditions of 34.5 kPa. It is not necessarily the same as solvents used in acrylic acid or lower-ester manufacture. An inorganic base, such as sodium hydroxide or ammonia, is used for neutralization of the ester mixture.

Storage for solvent used in 2-EHA manufacture requires a single tank farm tank sized for 60 days of storage. No working tankage is needed for the solvent. One tank is used to store 2-ethylhexanol and provides for 90 days of storage. No working tankage is needed. 2-ethylhexyl acrylate is stored in three tank farm tanks, each having 60 days of storage capacity. Eight working tanks having 1.75 days of storage are used to store 2-ethylhexyl acrylate. Table IV-1 summarizes the storage requirements for manufacture of 2-EHA and is based on data supplied by acrylic acid and ester manufacturers.[5]

The number of valves and pumps is discussed in Sect. IV.B. The number of fugitive emission sources is based on data received from acrylic acid and ester manufacturers.[5]

5. Inhibitor Unit of the Model Plant

A central inhibitor facility is used to store and mix the inhibitor for each process. Individual tankage is used to isolate the inhibitor for each ester.

Tankage for the inhibitor model plant consists of four tanks for ethyl acrylate inhibitor and the same for butyl acrylate and 2-ethylhexyl acrylate. The ethyl and butyl inhibitor tanks have 3 days of storage capacity and the ethylhexyl inhibitor tanks have 5 days of storage capacity. These data are based on information supplied by acrylic acid and ester manufacturers.[5]

The number of valves and pumps is discussed in Section IV.B. The number of fugitive emission sources is based on data received from acrylic acid and ester manufacturers.[5,6]

B. SOURCES AND EMISSIONS

Estimates of the uncontrolled emissions for the model plant are based on information received by virtually all the manufacturers of acrylic acid and esters. These data range from sample data for specific organics at specific process vents to material balance calculations. Overall, the estimate for uncontrolled emissions is expected to be accurate. Estimates of controlled emissions are based upon sparse sampled data from acrylic acid and esters plants.

The process emissions in the model plant are of two general categories: those emissions that vary linearly or nearly linearly with plant capacity (e.g., the quench-absorber off-gas), and those emissions that are constant or vary nonlinearly with capacity (e.g., losses from vacuum equipment). Vacuum equipment losses are functions of the air leaks into the equipment or the inert gas bled into the equipment to control the vacuum. These streams can vary from equipment to equipment, based on the vacuum pressure. Emissions from vacuum equipment are constant for each site since the air or inert leakage is independent of the production rate. However, these vacuum-related emissions vary from site to site as a function of the capacity ratio raised to the 0.65 power. This reflects the concept that large plants have larger vacuum equipment, which provides the same number of leak sites but a higher leak area per site.

Fugitive emissions are assumed constant regardless of production rate and plant capacity. Storage tank working losses vary linearly with production rate and capacity, while breathing losses are independent for capacity or production rate.

Secondary emissions from wastewater treatment can be a significant fraction of the total controlled emission levels. These values are based on key literature sources reporting VOC emissions from biochemical treatment plants. Further discussion of these calculations is presented in a separate EPA document concerning secondary emissions.[7]

1. Acrylic Acid Unit of the Model Plant

a. Quench-Absorber Off-Gas -- Stream 1A on Fig. III-1 represents the off-gas from the quench-absorber. This stream consists of air, propylene, unreacted organic feed materials (propane), and organic vapors from the product (acrylic acid) and by- products (acetic acid, acrolein, and others). Table IV-2 gives the composition of this stream from one manufacturer.[8]

This emission is assumed to be a linear function of the production rate since the inert-gas flow rate must be proportional to the amount of acrylic acid formed. Data from one manufacturer[8] indicate that the emission ratio of volatile organic compounds (VOC) to acrylic acid produced is 0.1193. This converts to 7157 Mg of VOC/yr for the model plant. This value is specific to a particular manufacturer but is expected to apply generally to all manufacturers of acrylic acid using propylene oxidation technology.

b. Combined Vents for Atmospheric Equipment -- Streams 1B and 1C on Fig. III-1 are vents from the atmospheric pressure sections of the acrylic acid equipment. The first, the extraction vent, has an emission relating to the normal operation of the extraction column. The second relates to noncondensables emitted from the raffinate stripper condenser. These emissions are combined and are assumed to be linear with production rate. Less than 9 Mg of VOC per year arises from this source for the model plant. Composition of this stream is shown in Table IV-3.

c. Combined Vents for Vacuum Equipment -- Streams 1D through 1G are all vents from vacuum distillation equipment. Vacuum control is achieved by bleeding nitrogen into each piece of equipment to maintain a specific pressure. This noncondensable gas carries some organic vapors with it as it leaves the condensers and vacuum system. After-condensers, or "tail" condensers, are typically used to

Table IV-2. Composition of Acrylic Acid Quench—Absorber Off-Gas in Model Plant[a]

Component	Weight Percent	Emission Ratio (kg/Mg)[b]
Acetaldehyde	<0.002	<0.1
Acetic acid	0.027	1.4
Acetone	0.025	1.3
Acrolein	0.087	4.5
Acrylic acid	0.347	18.0
Ethyl acrylate	0.023	1.2
Propane	1.45	75.3
Propylene	0.337	17.5
Water	1.71	88.6
Carbon dioxide	5.19	269.5
Carbon monoxide	2.28	118.5
Nitrogen	86.0	4466.6
Oxygen	2.48	128.8

[a] See ref 8.

[b] kg of component per Mg of acrylic acid.

Table IV-3. Composition of Combined Waste Gas from Vents from Acrylic Acid Atmospheric Pressure Equipment in Model Plant*

Component	Weight Percent
VOC	0.089
Carbon dioxide	18.59
Nitrogen	81.06
Carbon monoxide	0.26
Methane	0.002

[*] See ref. 5.

minimize organic losses to the vacuum system. Uncontrolled emissions in this study refer to the streams leaving the vacuum system after they have been passed through all the tail condensers.

These emissions are constant with production rate but are nonlinear functions of plant capacity and are adjusted to conform to the model plant capacity. Table IV-4 lists the individual compositions of these streams.

Streams 1D through 1G result in VOC emissions of 227 Mg/yr. Each manufacturing plant using the propylene oxidation process is assumed to have this emission regardless of capacity. Solvents having differing vapor pressures can significantly change this value.

d. Fugitive Emissions -- Process pumps, process valves, and relief valves are potential sources of fugitive emissions, even when operating on vacuum equipment, if static pressures are greater than atmospheric. Ten percent of the vacuum equipment fugitive sources are assumed to operate under positive pressures, thus generating fugitive emissions. Some 5/9 of the acrylic acid processing equipment is assumed to be atmospheric equipment. Thirty-six pumps (of which 18 are spares), 44 relief valves, and 820 process valves are assumed to be a typical case for acrylic acid manufacture.[5] All pumps operate on light liquids, all relief valves operate on gases and vapors, and all process valves operate on light liquids. The fugitive emission factors shown in Appendix C were applied in calculating the emissions listed in Table IV-5.

e. Storage Emissions -- Storage emissions for acrylic acid manufacture relate to tank farm and working storage for the acrylic acid extraction solvent and acrylic acid product. Propylene storage has no emissions since pressurized tanks are used to store propylene as a liquid. A hypothetical solvent having a molecular weight of 60 and a vapor pressure of 34.5 kPa at storage conditions is assumed. The storage required for acrylic acid working and tank farm tankage is presented in Table IV-1. These calculations are based on fixed-roof tanks, one-half full, and a 12.1°C diurnal temperature variation. Emission equations from AP-42 were used with one modification: the breathing losses were divided by 4 to account for recent evidence that indicates the AP-42 breathing loss equation overestimates emissions.[9,10] Weather conditions correspond to data

Table IV-4. Composition of Waste Gases from Extraction and Refining Vacuum Vents in Acrylic Acid and Esters Model Plant[a]

Component	Weight Percent	Emission Rate (kg/hr)
Extract Distillation Vent (Stream 1D)		
Hydrocarbon solvent	34.15	21.64
Acrylic acid	0.03	0.02
Carbon dioxide	1.19	0.754
Oxygen	1.12	0.710
Nitrogen	63.51	40.24
	Total	63.36
Foreruns Distillation Vent (Stream 1E)		
Hydrocarbon solvent	9.64	4.055
Acrylic acid	0.03	0.01
Oxygen	0.88	0.370
Nitrogen	89.31	37.55
Water	0.14	0.059
	Total	42.04
Acrylic Acid Distillation Vent[b] (Streams 1F and 1G)		
Hydrocarbon solvent	0.84	0.193
Carbon dioxide	0.16	0.036
Oxygen	3.45	0.795
Water	0.68	0.157
Nitrogen	94.87	21.85
	Total	23.03

[a] See ref. 5.

[b] Includes residue distillation.

Table IV-5. Total VOC Uncontrolled Fugitive Emissions in Acrylic Acid and Esters Model Plant

Process Unit*	Emission Rates (kg/hr) From Pumps	From Relief Valves	From Process Valves	Total
1	1.68	4.16	4.92	10.76
2	0.48	1.28	1.55	3.31
3	1.80	1.76	1.91	5.47
4	1.80	1.76	1.91	5.47
5	1.08	0.96	1.67	3.71
6	3.12	1.44	7.11	11.67
Total	9.96	11.36	19.07	40.4

*Numbers refer to Fig. IV-1 and are defined as follows:

1 = acrylic acid; 2 = inhibitor makeup; 3 = ethyl acrylate;

4 = butyl acrylate; 5 = 2-ethylhexyl acrylate; 6 = tank farm.

for the Houston, TX, area. Emissions calculated for a fixed-roof tank and presented in Table IV-6 include working and breathing losses.

f. Handling Emissions -- Handling emissions for acrylic acid manufacture include emissions relating to loading acrylic acid in drums, tank cars, tank trucks, and barges. The emissions are calculated from equations in AP-42.[9] A breakdown of the emissions from each loading source is presented in Table IV-7.

g. Secondary Emissions -- The following three secondary emissions relate to acrylic acid production: the spent catalyst, which requires regeneration or disposal; the wastewater from the quench-absorber, which is sent to a biological treatment plant; and finally, the liquid and solid organic residues, which are incinerated.

The emissions resulting from catalyst replacement are small. Care is taken to prevent the organic from being emitted.

The aqueous waste from acrylic acid plants has been reported to average 0.1041 g of VOC/g of acrylic acid produced and contains acrylic acid, polymers, inhibitor, acetic acid, and solvent.[11] The model plant will produce 11.1 Gg of dissolved VOC per year in its aqueous waste at a liquid flow of 50.6 m^3/hr (assuming a 2.5 wt % VOC concentration). VOC emissions of from 0.1 to 3.7 Mg/yr are estimated to be produced during biooxidation of this waste. The value shown in Table IV-8 is 0.208 kg/hr, or 1.8 Mg/yr, and represents a reasonable level, considering the specific components. Concentrations of solvents with a high relative volatility can markedly increase the secondary emissions from this source.[7]

Information about the generation of liquid residues is generally sensitive to the acrylic acid manufacturers. These residues are often used as supplementary fuel for steam-generating incineration units.[8] Emissions from this source are considered as controlled emissions in the discussion in Sect. V.

Generation of solid residues is related to a process upset, where some of the acrylic acid polymerizes at random intervals. About 4.5 Mg/yr of solid acrylate polymer residue is assumed to be generated by the model plant. Emissions

Table IV-6. Total VOC Uncontrolled Storage Emissions for Fixed-Roof Tanks

	Emission Rates (kg/hr)[b]		
Process Unit[a]	From Working Tanks	From Tank Fram Tanks	Total
1	0.431	0.539	0.97
2	0.871[c]	7.30[d]	8.17
4	0.416[c]	2.62[d]	3.04
5	0.005[c]	0.069	0.07
Total	1.72	10.53	12.3

[a] Numbers refer to Fig. IV-1 and are defined as follows:

1 = acrylic acid; 3 = ethyl acrylate; 4 = butyl acrylate;
5 = 2-ethylhexyl acrylate.

[b] Includes working and breathing losses.

[c] Inhibitor working tank emissions included.

[d] Single solvent storage tank emission prorated against processes 3 and 4.

Table IV-7. Total VOC Uncontrolled Handling Emissions in Acrylic Acid and Esters Model Plant

Process Unit[a]	Emission Rate[b] (kg/hr)			
	From Drums[c]	From Tank Car and Tank Truck	From Barge	Total
1	0.0006	0.0033	0.0017	0.006
3	0.043	0.261	0.130	0.434
4	0.0059	0.033	0.017	0.056
5	0.0001	0.0006	0.0003	0.001
Total	0.050	0.298	0.149	0.497

[a] Process numbers refer to Fig. IV-1 and are defined as follows: 1 = acrylic acid; 3 = ethyl acrylate; 4 = butyl acrylate; 5 = 2-ethylhexyl acrylate.

[b] The following loading ratios of each product are assumed: of every 10 m^3 of each product loaded, 1 m^3 is drummed, 3 m^3 is loaded into barges, and 6 m^3 is loaded into tank cars or tank trucks.

[c] Loading losses for drumming were assumed to possess the same "saturation factor" (see ref. 9) as those for tank car, tank truck, and barge; saturation factor, S = 0.5.

Table IV-8. Total VOC Uncontrolled Secondary Emissions in Acrylic Acid and Esters Model Plant

Process Unit[a]	Emission Rate (kg/hr)		
	From Wastewater[b]	From Residues[c]	From Sulfuric Acid Recovery[d]
1	0.014—0.428 0.208	0.005	None
3,4,5	0.011—0.332 0.155	0.005	41.8
Total	0.025—0.760 0.363	0.010	41.8

[a] Process numbers refer to Fig. IV-1 and are defined as follows: 1 = acrylic acid; 3 = ethyl acrylate; 4 = butyl acrylate; 5 = 2-ethylhexyl acrylate.

[b] See ref 7.

[c] Emissions from residue incineration.

[d] See ref. 6.

[e] This value used in data in following tables.

arising from the incineration of this material contribute 0.045 Mg of VOC per year. The solids incinerator burning this material is a unit servicing more than this acrylate plant. It has primary and secondary combustion chambers and operates at 99% VOC removal.

Secondary emissions for the acrylic acid plant are presented in Table IV-8.

2. EA Unit of the Model Plant

Emissions from the model plant are discussed in the following sections. However, one manufacturer producing ethyl acrylate by a confidential process reports total ethyl acrylate process emissions of 0.0425 g of VOC per g of ethyl acrylate.[8] Other manufacturers' processes are expected to be similar to the model plant in emissions.

a. Combined Vents from Atmospheric Equipment -- Streams 3A through 3C on Fig. III-2 represent emissions from equipment used in the production of ethyl acrylate by direct esterification. All these emissions originate from noncondensable gases passing through condensers in these atmospheric-pressure distillations. These emissions together contribute 0.00054 g of VOC/g of ethyl acrylate produced and the amount is assumed to be linear with production rate. This converts to 21.1 Mg of VOC per year for the model plant. The composition of this combined stream is shown in Table IV-9.

b. Combined Vents from Vacuum Equipment -- Streams 3D through 3F on Fig. III-2 result from noncondensable gases passing through condensers in vacuum distillation equipment. These emissions together contribute 148 Mg of VOC per year and are a nonlinear function of capacity. Table IV-10 shows the composition of this combined stream.

c. Fugitive Emissions -- Process pumps, process valves, and relief valves are potential sources of fugitive emissions. Even pumps and valves operating on vacuum equipment may contribute to fugitive emissions if they operate in locations having static pressures greater than atmospheric.

Ten percent of pumps, valves, and relief valves operating on vacuum equipment are expected to have fugitive losses. Some 5/8 of the ethyl acrylate process

Table IV-9. Composition of Waste Gases from Vents from Ethyl Acrylate Atmospheric Equipment in Model Plant*

Component	Weight Percent
Denaturant	0.19
Ethyl acrylate	2.43
Ethyl ether	0.20
Ethanol	1.70
Oxygen	13.00
Nitrogen	79.57
Water	1.09
Methane	1.82

*See ref. 5.

Table IV-10. Composition of Waste Gases from Vents from Ethyl Acrylate Vacuum Equipment in Model Plant*

Component	Weight Percent	Emission Rate (kg/hr)
Ethyl acrylate	0.74	2.77
Denaturant	1.55	5.82
Ethyl ether	2.02	7.57
Ethanol	0.18	0.68
Oxygen	2.94	11.03
Nitrogen	91.65	343.8
Water	0.92	3.45
	Total	375.1

*See ref. 5.

equipment is assumed to be atmospheric equipment. Twenty-two pumps (11 of which are spares), 16 relief valves, and 288 process valves are assumed to be typical numbers for ethyl acrylate manufacture.[5] All pumps operate on light liquids, all relief valves operate on gases and vapors, and all process valves operate on light liquids. Fugitive emission factors, as shown in Appendix C, are applied to calculate the fugitive emissions shown in Table IV-5.

d. Storage Emissions -- Storage emissions for ethyl acrylate manufacture relate to tank farm and working storage for ethyl acrylate solvent, ethyl acrylate, and ethanol. A hypothetical solvent having a molecular weight of 60 and a vapor pressure of 34.5 kPa at storage conditions is assumed. The storage required for ethyl acrylate working and tank farm storage is presented in Table IV-1. Emission calculations are based on fixed-roof tanks, half full, a 12.1% diurnal temperature variation. Emission equations from AP-42 were used with one modification: the breathing losses were divided by 4 to account for recent evidence that indicates the AP-42 breathing loss equation overestimates emissions.[9,10] Weather conditions correspond to data from the Houston, TX, area. Emissions calculated for fixed- roof tanks and presented in Table IV-6 include working and breathing losses.

e. Handling Emissions -- Handling emissions for ethyl acrylate manufacture include emissions relating to loading ethyl acrylate in drums, tank cars, tank trucks, and barges. The emissions are calculated from equations in AP-42.[9] A breakdown of the emissions from each loading source is presented in Table IV-7.

f. Secondary Emissions -- There are three secondary emissions related to acrylic ester production: spent acid, which is recovered; other wastewater, which is disposed of in biochemical treatment plants; and organic liquids and solids, which are incinerated.

Emissions from a sulfuric acid concentrator for one manufacturer are limited to 113 kg/hr by local regulations.[6] The unit operates about 90% of the time on acid from acrylate ester production. About 5.5 g of VOC/kg of acrylate ester may be expected, which amounts to 366 Mg/yr of VOC from acid recovery.

Total organic carbon in the aqueous waste from acrylic ester manufacture is reported as 30.8 g per kg of acrylates manufactured.[12] If this carbon is assumed to be a 3-carbon compound with a molecular weight of 85, then 72.7 g of VOC/kg of total acrylate (excluding acrylic acid capacity), or 4.84 Gg/yr, is generated from the model plant. The emissions related to this wastewater range from 0.1 to 2.9 Mg/yr for the model plant. The expected value, estimated to be 0.155 kg/hr, or 48.4 Mg/yr, is shown in Table IV-8. Further information is given in a separate EPA report.[7]

The model plant is assumed to produce 4.5 Mg/yr of organic solids for incineration. The VOC emission resulting from this material is 0.045 Mg/yr. Liquid organic waste streams are incinerated in heat-recovery incinerators as supplemental fuel. This incinerator is discussed in Sect. V.

Secondary emissions are summarized in Table IV-8.

3. BA Unit of the Model Plant

a. Process Emissions -- Process emission sources for BA are assumed to be similar to those produced in manufacturing ethyl acrylate. A manufacturer of BA reports emissions of 0.0008 g of VOC/g of BA produced.[8] The composition of the combined streams is shown in Table IV-11. Emissions for the model plant are 19.1 Mg/yr. It is assumed that 14% of the emissions arises from atmospheric equipment, similar to that used in producing EA.

b. Fugitive Emissions -- Fugitive emissions for BA are assumed to be similar to those in the manufacture of EA. These are shown in Table IV-5.

c Storage Emissions -- Storage emissions for BA manufacture relate to tank farm and working storage for BA solvent, BA, and butanol. The solvent is the same as that used for EA manufacture and shares tank farm tankage with the EA solvent. Emission calculations are based on fixed-roof tanks, half full, a 12.1°C diurnal temperature variation. Breathing losses were modified as previously indicated.[9,10] Weather conditions correspond to data from the Houston, TX, area. Emissions calculated for fixed-roof tanks, presented in Table IV-6, include working and breathing losses.

Table IV-11. Composition of Combined Waste Gas from All Butyl Acrylate Equipment in Acrylic Acid and Esters Model Plant*

Components	Weight Percent
Butyl acrylate	1.83
Butanol	1.83
Water	8.68
Air	87.60

*See ref 8.

d. Handling Emissions -- Handling emissions for BA manufacture include those relating to loading BA in drums, tank cars, tank trucks, and barges. The emissions are calculated from equations in AP-42.[9] A breakdown of the emissions from each loading source is presented in Table IV-7.

e. Secondary Emissions -- Secondary emissions for all acrylate ester manufacture are discussed in Sect. IV.B.2.f.

4. 2-EHA Unit Model of the Plant

a. Combined Vents from Atmospheric Equipment -- Stream 5A on Fig. III-3 vents noncondensable gases from the condensers on the esterification reactor-distillation. Stream 5B on Fig. III-3 vents the neutralizer. These emissions are assumed to be linear with production rate. The organic emission related to these streams is 0.00488 g of VOC/g of 2-EHA. The average composition is shown in Table IV-12. About 31.8 Mg of VOC per year arises from this source.

b. Combined Vents from Vacuum Equipment -- Streams 5C through 5E on Fig. III-3 correspond to noncondensable gases passing through the condensers on the 2-EHA vacuum refining distillations. These emissions are assumed to be a nonlinear function of capacity and contribute 16.6 Mg/yr of VOC. The average compositions for these streams are shown in Table IV-13.

c. Fugitive Emissions -- Process pumps, process valves, and relief valves are potential sources of fugitive emissions. Even pumps, relief valves, and valves operating on vacuum equipment may contribute to fugitive emissions if they operate in locations having static pressures greater than atmospheric.

It is assumed that 10% of the pumps, process valves, and relief valves operating on vacuum equipment will have fugitive losses. Two-fifths of the 2-EHA process equipment is assumed to be atmospheric equipment. Twenty-two pumps (of which 11 are spares), 13 relief valves, and 363 process valves are assumed to be typical numbers for 2-EHA manufacture.[5] All pumps operate on light liquids, all relief valves operate on gases and vapors, and all process valves operate on light liquids. Fugitive emission factors, shown in Appendix C, were applied to calculate the fugitive emissions shown in Table IV-5.

Table IV-12. Composition of Waste Gases from Vents from 2-EHA Atmospheric Equipment in Acrylic Acid and Esters Model Plant*

Component	Weight Percent
Hydrocarbon solvents	13.96
Ethyl ether	1.60
"Light boiler"	1.28
Carbon dioxide	0.14
Argon	0.26
Oxygen	6.40
Nitrogen	75.78
Water	0.74
Methane	0.11

*See ref 5.

Table IV-13. Composition of Waste Gases from Vents from 2-EHA Vacuum Equipment in Acrylic Acid and Esters Model Plant*

	Emissions	
Component	(wt %)	(kg/hr)
Several light organic unknowns	9.47	1.89
Argon	0.61	0.12
Oxygen	11.56	2.24
Nitrogen	77.48	15.03
Water	0.61	0.12
Total		19.40

*See ref 5.

d. Storage Emissions -- Storage emissions for 2-EHA manufacture relate to tank farm and working storage for 2-EHA solvent, 2-ethylhexanol, and 2-EHA. A hypothetical solvent having a molecular weight of 60 and a vapor pressure of 34.5 kPa at storage conditions is assumed. The storage required for 2-EHA working and tank farm storage is presented in Table IV-1. Emission calculations are based on fixed-roof tanks, half full, a 12.1% diurnal temperature variation. Emission equations from AP-42 were used with one modification: breathing losses were modified as previously indicated.[9,10] Weather conditions correspond to data from the Houston, TX, area. Emissions calculated for fixed-roof tanks and presented in Table IV-6 include working and breathing losses.

e. Handling Emissions -- Handling emissions for 2-EHA manufacture include emissions relating to loading 2-EHA in drums, tank cars, tank trucks, and barges. The emissions are calculated from equations in AP-42.[9] A breakdown of the emissions from each loading source is presented in Table IV-7.

f. Secondary Emissions -- Secondary emissions for all acrylate ester manufacture are discussed in Sect. IV.B.2.f.

5. Inhibitor and Tank Farm Units of the Model Plant

Figure IV-1 shows an integrated acrylates facility including inhibitor makeup and tank farm, with which fugitive emissions are related. The inhibitor model plant has 4 pumps (of which 2 are spares), 8 relief valves, and 155 process valves. The tank farm has 26 pumps (of which 13 are spares), 9 relief valves, and 711 process valves.[5]

Storage emissions in the inhibitor model plant and the tank farm are prorated against the process that they serve.

6. Total Model Plant Uncontrolled Emissions

Table IV-14 shows the uncontrolled emissions for the integrated acrylate model plant; stream designations refer to Fig. IV-1.

Table IV-14. Total Uncontrolled VOC Emissions from Acrylic Acid and Esters Integrated Model Plant

Source	Stream Designation	Emission Ratio (g/kg of product[a])	Emission Rate (kg/hr)
Acrylic acid quench-absorber off-gas	1A	119.3	817
Combined Vents			
From acrylic acid atmospheric equipment	1B,1C	0.146	<1
From acrylic acid vacuum equipment	1D,1E,1F,1G	3.78[b]	25.9
From ethyl acrylate atmospheric equipment	3A,3B,3C	0.54	2.41
From ethyl acrylate vacuum equipment	3D,3E,3F	3.79[b]	16.9
From all butyl acrylate equipment	4A,4B,4C,4D,4E,4F	0.90[c]	2.18
From 2-EHA atmospheric equipment	5A,5B	4.88	3.63
From 2-EHA vacuum equipment	5C,5D,5E	2.54[b]	1.89
Storage			
Working	1H,3H,4H,5H	0.20[d]	1.72
Tank farm	1H,3H,4H,5H	1.20[d]	10.5
Fugitive	1I,2I,3I,4I,5I,6I	4.62[b]	40.4
Handling	1J,3J,4J,5J		
Drum loading			0.050
Tank car/truck loading		0.06[d]	0.298
Barge loading			0.149
Secondary			
Wastewater	1K,3K,4K,5K	0.04[d]	0.363
Organic residues	1K,3K,4K,5K	0.001[b]	0.010
Sulfuric acid recovery	1K,3K,4K,5K	4.78[d]	41.8
		Total	966

[a] Based on model plant capacities of each product, unless otherwise noted.

[b] Constants or independent of production rate; nonlinear function of capacity; valid only for model plant.

[c] Data adjusted by assuming 14% of total corresponds to atmospheric equipment, which varies linearly with capacity, and the remainder corresponds to vacuum equipment, which varies nonlinearly with capacity.

[d] Based on total acrylates capacity (76.59 Gg/yr).

C. REFERENCES*

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. ACRYLIC ACID FROM PROPYLENE AND ESTERS BY DIRECT ESTERIFICATION - INTEGRATED PLANT

1. Thermal Oxidizer

The current practice for emission control in the manufacture of acrylic acid and esters is the use of a liquid-fume thermal oxidizer to burn organic emissions from an integrated plant. This unit typically incorporates heat recovery and thus becomes an energy source for the acrylates processing plant or other plants on-site.[1--3] This control device has been necessary because of the extreme odor-causing nature of acrylic acid and its esters. In addition, it is necessary to destroy toxic materials such as acrolein that are present in the manufacture of acrylic acid.

The integrated acrylates model plant, as shown in Fig. IV-1, will utilize a liquid-fume thermal oxidizer as the major applicable control device. Vents from acrylic acid, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, inhibitors, and loading will be routed to an incinerator in a series of vent manifolds. Figure V-1 shows the collection system and material balance for this control device.

a. Process Emissions -- The major organic emission from the integrated model plant arises from the propylene oxidation quench-absorber. This stream is a relatively constant emission source and is labeled Stream 1A or I on the flow diagram of Fig. V-1.

Emissions from atmospheric pressure equipment are combined from acrylic acid, ethyl acrylate, butyl acrylate, and 2-ethylhexyl acrylate processing units. Stream II of Fig. V-1 shows the total VOC contribution from these vents.

Emissions from vacuum processing equipment arise from the acrylic acid, ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate processing units. These emissions largely arise from nitrogen gas bled into the equipment to control the vacuum pressure. Vacuum equipment typically is designed to utilize several condensers in series on the uncondensed gases leaving the equipment. Secondary

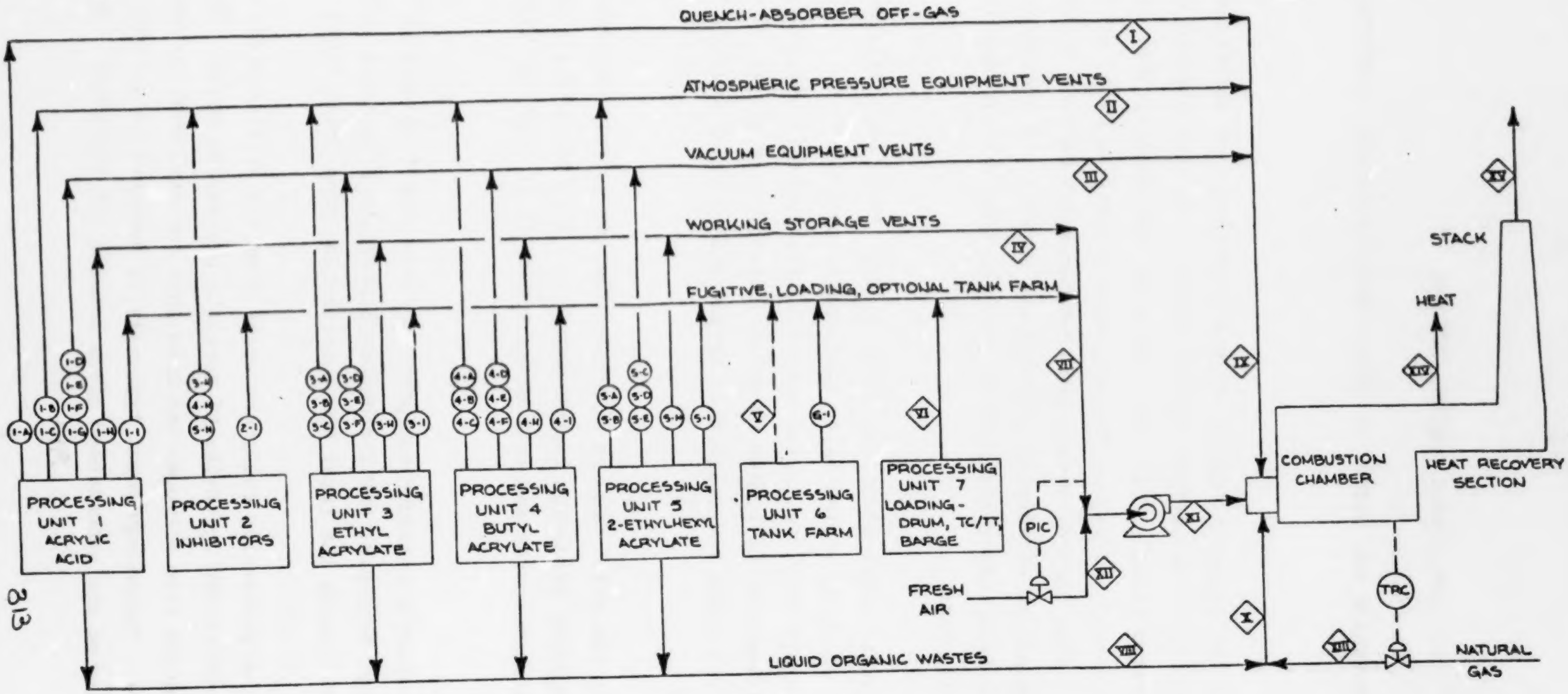
QUENCH-ABSORBER OFF-GAS
ATMOSPHERIC PRESSURE EQUIPMENT VENTS
VACUUM EQUIPMENT VENTS
WORKING STORAGE VENTS
FUGITIVE, LOADING, OPTIONAL TANK FARM
LIQUID ORGANIC WASTES
I
II
III
IV
V
VI
VII
VIII
IX
X
XI
XII
XIII
XIV
XV
1-A
1-B
1-C
1-D
1-E
1-F
1-G
1-H
1-I
3-H
4-H
5-H
2-I
3-A
3-B
3-C
3-D
3-E
3-F
3-H
3-I
4-A
4-B
4-C
4-D
4-E
4-F
4-H
4-I
5-A
5-B
5-C
5-D
5-E
5-H
5-I
6-I
PROCESSING UNIT 1 ACRYLIC ACID
PROCESSING UNIT 2 INHIBITORS
PROCESSING UNIT 3 ETHYL ACRYLATE
PROCESSING UNIT 4 BUTYL ACRYLATE
PROCESSING UNIT 5 2-ETHYLHEXYL ACRYLATE
PROCESSING UNIT 6 TANK FARM
PROCESSING UNIT 7 LOADING - DRUM, TC/TT, BARGE
PIC
FRESH AIR
COMBUSTION CHAMBER
HEAT RECOVERY SECTION
HEAT
STACK
TRC
NATURAL GAS

Fig. V-1. Liquid-Fume Thermal Oxidizer for Acrylic Acid and Ester Model Plant

condensers remove some additional VOC that may have passed through the main condenser. These additional control devices are "in series" with the major control device -- the thermal oxidizer. They are not the best control option, since organic reduction by use of condensers alone will not abate the odor problem; therefore combustion of the streams after the condensers is practiced. Emissions shown on Fig. V-1 as uncontrolled emissions are therefore defined as the emissions leaving the last secondary condenser before entering the thermal oxidizer.

b. Working Storage Emissions -- This integrated acrylates facility has both working storage (or process tanks) and tank farm storage (for bulk storage) as shown in Table IV-1. The working storage losses will be collected in a suction header, combined with other emissions, and sent to the thermal oxidizer for use as combustion air. The vent from each tank discharges into the base of a conical pipe leading to the suction manifold. The suction is supplied by the suction side of a blower delivering combustion air to the thermal oxidizer. Each conical ending is individually designed to allow sufficient air to enter the manifold to capture all the organic emission from the tank at the greatest instantaneous flow rate of the tank emission and to dilute the organic below the lower explosive limit. Pressure drops in all the manifold legs are considered and Lower Explosion Limit (LEL) monitors are used to maintain nonexplosive conditions in the manifold. Emissions shown on Fig. V-1 assume that all streams collected in the suction manifold have VOC concentrations of 50% of the lower explosive limit for ethyl acrylate. The LEL for ethyl acrylate is reported to be 1.8 vol %.[4]

Storage tank emissions are discussed later.

c. Fugitive Emissions -- Fugitive emissions can occur in the integrated model plant even though much of the equipment is operated under vacuum. Important sources of fugitive losses are collected in the suction manifold discussed above. Fugitive emissions occurring in enclosed areas, where the air flow may be controlled are included in the suction manifold. Process sumps or equipment inside the buildings are examples of this.

Fugitive emissions shown on Fig. V-1 are assumed to be controlled emissions (major leaks detected and repaired and mechanical seals on pumps) as defined in Appendix C. Many of the pumps, relief valves, or process valves are on equipment that is located outdoors. These potential fugitive emission sources are impractical for inclusion in the suction manifold. Therefore the collected fugitive emissions used in Fig. V-1 are assumed to be 50% of the controlled fugitive emissions calculated as described in Appendix C. The remainder are assumed to be emitted to the atmosphere and are shown as uncollected fugitive emissions on Table V-1.

d. Handling Emissions -- Emissions from loading acrylic acid and esters in drums, tank cars, tank trucks, and barges are small and probably would not require control on the basis of VOC alone. However, odor and toxicity problems require more stringent control techniques than those mandated by VOC control alone.

In the model plant it is assumed that all loading locations are within close proximity to the acrylic acid and esters unit so that these emissions can be included in the suction manifold. These emissions are shown as Stream VI on Fig. V-1.

When the loading stations are significantly distant from the thermal oxidizer, on-site control devices such as vapor recovery, fume incineration, and other techniques may be used for occupational health and odor control. Costs for these devices will not be included since their use is mandated by guidelines other than VOC reduction.

e. Secondary Emissions -- The integrated model plant produces significant quantities of liquid organic wastes that are burned in the thermal oxidizer. These wastes are shown as Stream VIII on Fig. V-1.

f. Supplementary Combustion Air and Fuel -- The oxygen needed for combustion is supplied by the oxygen in the organic molecules and by suction manifold air. Additional air is fed as required into the suction side of the blower discharging into the thermal oxidizer.

Table V-1. Total VOC Controlled Emissions for Integrated Acrylic Acid and Ester Model Plant Acrylic Acid by Propylene Oxidation, Esters by Direct Esterification

Source	Stream Designation (Fig. IV-1)	Control Device	Emission Reduction (%)	Emission Ratio (Based on Total Acrylates) (g/Mg)	Emission Rate (kg/hr)
Quench-absorber off-gas	1A	Thermal oxidizer	99+[a]	934	8.17
Atmospheric pressure equipment vents	1B, 1C 3A, 3B, 3C 4A, 4B, 4C 5A, 5B, 5C	Thermal oxidizer	99+	8	0.073
Vacuum equipment vents	1D, 1E, 1F, 1G 3D, 3E, 3F 4D, 4E, 4F 5C, 5D, 5E	Thermal oxidizer	99+	53[b]	0.46
Working storage	1H, 2H, 3H, 4H, 5H (from each processing unit)	Thermal oxidizer	99+	2[b]	0.020
Tank farm storage	1H, 3H, 4H, 5H (from processing unit 6)	Covered floating-roof tanks	85[c]	181[b]	1.58
Collected fugitives[d]	1I, 2I, 3I, 4I, 5I, 6I	Thermal oxidizer	99+	9[b]	0.063
Uncollected fugitives[e]	1I, 2I, 3I, 4I, 5I, 6I	None	None	721[b]	6.3
Handling-loading	1H, 3H, 4H, 5H (from processing unit 7)	Thermal oxidizer	99+	1	0.005
Secondary					
Wastewater	8K	None	None	42	0.363
Liquid organic residues	9K	Thermal oxidizer	99+	1247	10.9
Solid organic residues	9K	Solid waste incinerator	99+	1	0.01
Sulfuric acid recovery	10K	None	None	4781	41.8
Total					69.7

[a] Efficiency of 99+ is calculated as 99.0 although higher efficiencies are possible.

[b] Valid only for model plant at capacity; nonlinear or constant with plant capacity.

[c] Based on total VOC emissions for all model plant tank farm storage; 4 tanks have covered floating roofs.

[d] Calculated based on Appendix C as "controlled fugitive losses." Assumes 50% of fugitive losses are collected in suction manifold.

[e] Assumes 50% of controlled fugitive losses cannot be collected in suction manifold.

The thermal oxidizer runs at essentially constant temperature by supplying supplementary fuel as natural gas when the VOC in the waste streams (Streams VIII, IX, and XI on Fig. V-1) falls below that necessary to maintain the combustion temperature. Also, when VOC surges occur, the supplementary fuel flow is reduced to lower the combustion temperature and conserve energy.

g. Heat Recovery -- Nearly two-thirds of the heat leaving the combustion chamber is recovered based on a flue gas calculation in which it is assumed that the flue gas temperature is 260°C (500°F). Two percent of the heat is assumed to be lost as radiation from the combustion chamber. The recovered heat is used elsewhere in the acrylate plant or in other plants in the area and is shown as Stream XIV on Fig. V-1.

2. Storage - Tank Farm

Floating-roof tanks are used to control storage tanks with 40,000 gal or larger capacity and for storing materials with vapor pressures greater than 0.5 psig at storage conditions. Four tanks listed in Table IV-1 are candidates under this criterion: the 981.8-m^3 acrylic acid solvent tank, the 8521.0-m^3 EA-BA solvent tank, the 4396.0-m^3 ethanol tank, and the 6941.0-m^3 ethyl acrylate tank.

Because of the odor considerations the ethyl acrylate storage tank is a candidate for inclusion into the suction manifold and can be routed to the thermal oxidizer. If the tank farm is in close proximity to the thermal oxidizer, all tanks may be vented into the suction manifold, providing a second control device in series, i.e., internal-floating-roof tanks* in series with the thermal oxidizer. These varying levels of control for tank farm storage are shown in Table E-1 in Appendix E. The case of internal-floating-roof tanks alone is shown as Stream V on Fig. IV-1 as an optional feed to the thermal oxidation unit but is not included in the thermal oxidizer feed.

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*Consist of internal floating covers or covered floating roofs as defined in API 25-19, 2d ed., 1976 (fixed-roof tanks with internal floating device to reduce vapor loss).

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3. Fugitive Sources

Controls for fugitive sources, not included in the thermal oxidizer feed, will be included in a future EPA document that discusses fugitive emissions from the synthetic organic chemicals manufacturing industry. Emissions from pumps and valves can be controlled by an appropriate leak-detection system with mechanical seal pumps plus repair and maintenance as needed. Repair of leaks in acrylic acid and ester plants may already include the techniques necessary for controlled fugitive emissions.[2,3] Therefore controlled emissions are assumed on Fig. V-1 and Table V-1. Factors used in calculating the controlled fugitive emissions are presented in Appendix C.

4. Secondary Sources

Secondary emissions caused by wastewater treatment of aqueous wastes in acrylic acid and ester plants can be significant. The presence of organic compounds possessing high relative volatilities (compared with water) and/or low aqueous solubilities can result in emissions much larger than those shown on Table V-1.

Recovery of sulfuric acid can also generate significant organic emissions. The value shown in Table V-1 is based upon the emission rate of a sulfuric acid recovery unit serving acrylic acid and ester and methyl methacrylate plants.[3] Control of secondary emissions will be discussed in a future EPA report. No control system has been identified for the secondary emissions from the model plant.

B. ACRYLIC ACID BY HIGH-PRESSURE MODIFIED REPPE PROCESS

Control devices required by the high-pressure modified Reppe process are shown on Table V-2. The control technology is different from the propylene oxidation process since the high-pressure modified Reppe process utilizes the highly volatile and water-soluble solvent, tetrahydrofuran. It is anticipated that this process will be replaced by the propylene oxidation process in the early 1980s.

C. REFERENCES*

1. R. W. Serth, D. R. Tierney, and T. W. Huges, Source Assessment: Acrylic Acid Manufacture State-of-the-Art (on file at EPA, IERL, Cincinnati, OH) (1978).
2. J. W. Blackburn, IT Enviroscience, Trip Report on Site Visit to Union Carbide Corp., South Charleston, WV Dec. 8, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
3. J. W. Blackburn, IT Enviroscience, Trip Report on Site Visit to Rohm and Haas Co., Deer Park TX, Nov. 1, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
4. J. W. Nemec and W. Bauer, Jr., "Acrylic Acid and Derivative," pp. 330--354 in Kirk-Othmer Encyclopedia of Chemical Technology, 3d ed., Wiley, New York, 1978.
5. Nonconfidential information received May 1978 from Celanese Chemical Co., Houston, TX (on file at EPA, ESED, Research Triangle Park, NC).
6. Texas State Emission Inventory Questionnaires (1975) for Dow Badische, Freeport, TX (on file at EPA, ESED, Research Triangle Park, NC).

*Usually, when a reference number is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. CONTROL COST IMPACT

This section presents estimated costs and cost effectiveness data for control of total VOC emissions resulting from the production of acrylic acid and esters. Details of the integrated model plant (Fig. IV-1) are given in Sects. III and IV. Cost estimate calculations are included in Appendix D.

Capital cost estimates represent the total investment required to purchase and install all equipment and material required to provide a complete emission control system performing as defined for a new plant at a typical location excluding costs related to the suction manifold. They do not include the cost of acrylic acid or ester production lost during installation or startup, of research and development, or of land acquisition.

Bases for the annual cost estimates for the control alternatives include utilities, operating labor, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. These costs are developed in the thermal oxidizer control device evaluation.[1] Cost factors used are itemized in Table VI-1.

1. Emission Control for Process, Working Storage, Fugitive, Loading, and Liquid Organic Wastes

Emissions from the acrylic acid, lower-, and heavy-ester plants are combined as shown on Fig. V-1 and fed to a specially designed thermal oxidizer. This unit receives fumes from the quench-absorber off-gas, combined atmospheric equipment vents, and combined vacuum equipment vents. A specially designed suction manifold system collects emissions from working storage tanks and loading areas and some fugitive sources, combines the contaminated air with fresh air, and discharges the mixture into the combustion chamber as combustion air. It may be possible to include tank farm storage emissions in this collection system. In this report floating-roof tanks are the applicable control method for large storage tanks and these storage emissions will not be fed to the thermal oxidizer.

Table VI-1. Annual Cost Parameters

Operating factor	8760 hr/yr[a]
Operating labor	$15/man-hr
Fixed costs	
Maintenance labor plus materials, 6%	29% of installed capital cost
Capital recovery, 18%[b]	
Taxes, insurances, administration charges, 5%	
Utilities	
Process water	$\$0.07/\text{m}^3$ ($0.25/thousand gal)
Electric power	$8.33/GJ ($0.03/kWh)
Steam	$5.50/Mg ($2.50/thousand lb or million Btu)
Natural gas	$\$1.90/\text{GJ}$ ($\$2.00/\text{thousand ft}^3$ or million Btu)
Heat recovery credits (equivalent to natural gas)	$1.90/GJ ($2.00/million Btu)

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[a] Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculation the error introduced by assuming continuous operation is negligible.

[b] Based on 10-year life and 12% interest.

Liquid organic wastes are burned in the thermal oxidizer and supply some fuel value. Natural gas is used as supplemental fuel. VOC reductions of 99% are expected for the fumes, the organic collected in the suction manifold, and the liquid organic wastes.

Capital costs for the liquid-fume thermal oxidation unit for the acrylic acid and ester model plant depend on the temperature of combustion and on whether it includes heat recovery. A unit operating at 1400°F will cost $730,000 without heat recovery and $1,050,000 with heat recovery. A unit operating at 1600°F will cost $830,000 without heat recovery and $1,270,000 with heat recovery. Heat recovery is a waste-heat boiler generating 250-psi steam. These values do not include the cost for the suction manifold system to collect the working storage, fugitive, and loading emissions. The cost of this system is dependent on the plant configuration and is difficult to predict.

Figures VI-1 to VI-3 present capital and net annual costs, as well as cost effectiveness, for the thermal oxidizer as a function of plant capacity. Table VI-2 shows the emission-control costs and the cost effectiveness data for the thermal oxidizer in the acrylic acid and ester model plant.

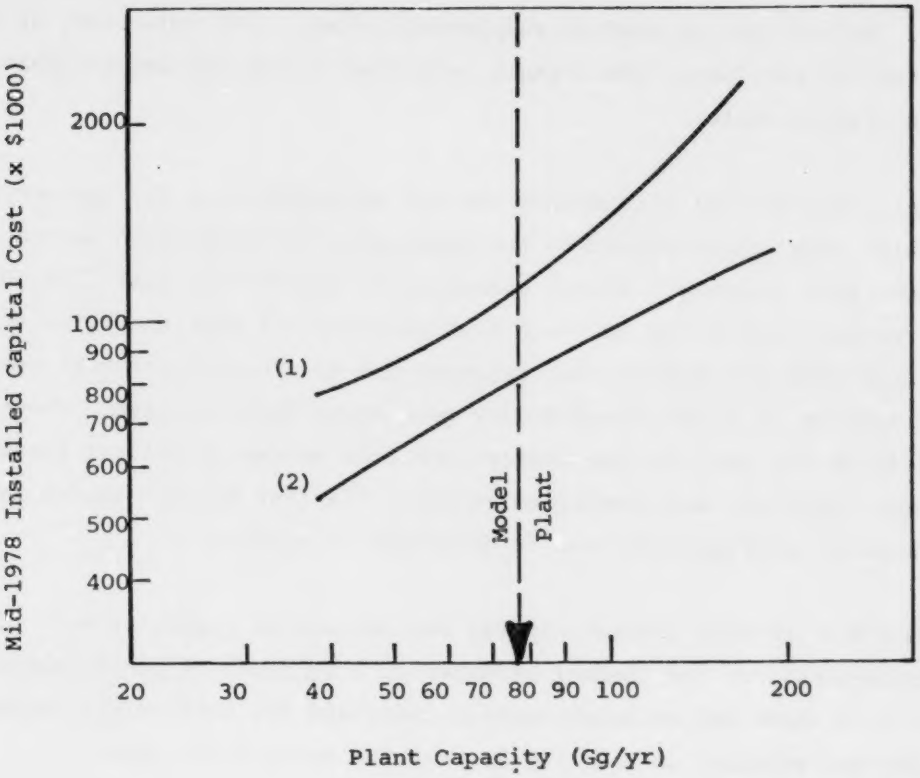
Costs for internal-floating-roof tanks with contact-type double seals are presented in another EPA report covering storage tanks.[2]

3. Secondary Emissions

a. Solid Organic Wastes -- Solid organic wastes generated in the acrylic acid and esters integrated model plant are burned in an independent solid-waste incinerator with secondary combustion. This unit serves more than just the acrylic acid and esters plants. Therefore cost analysis of this unit will not be prepared. Organic reduction efficiency is assumed to be greater than 99%.

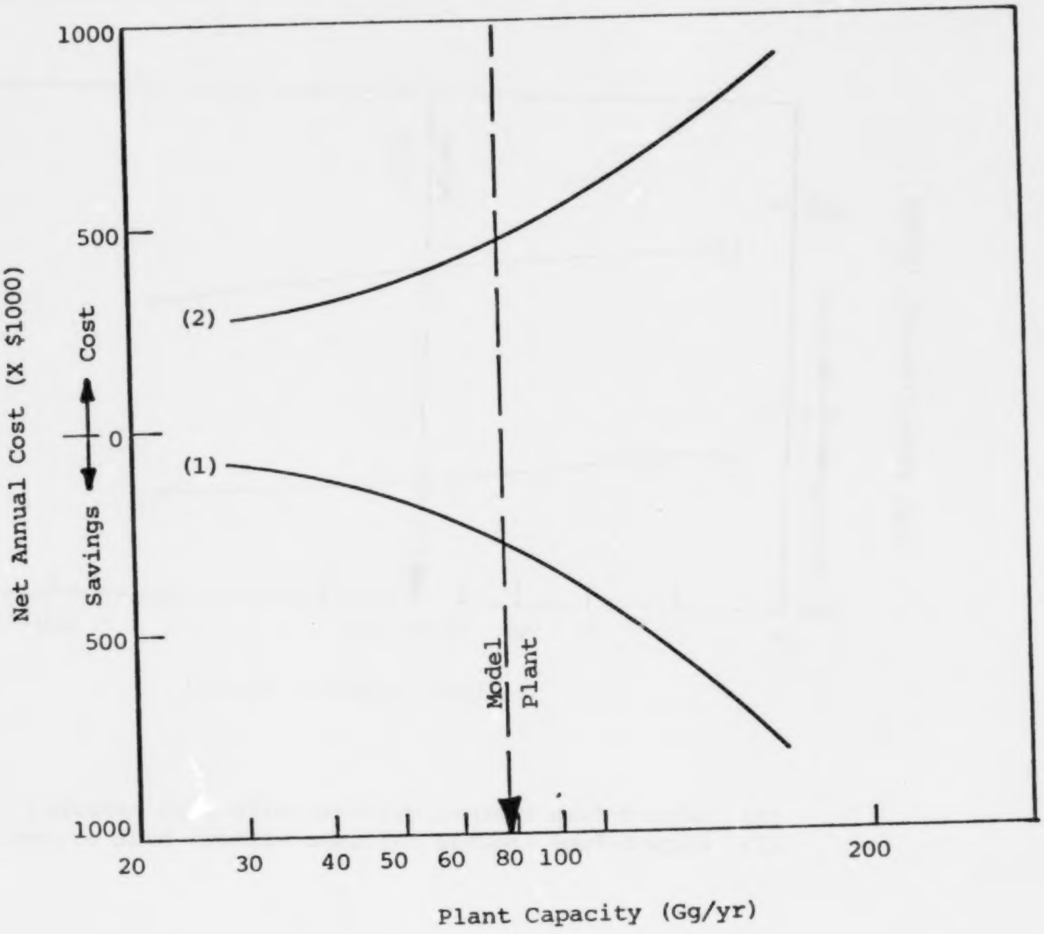
b. Wastewater -- The control of emissions from wastewater will be discussed in a future EPA document.

c. Sulfuric Acid Recovery -- Emissions from sulfuric acid recovery can be a significant fraction of the controlled emissions from the acrylic acid and esters



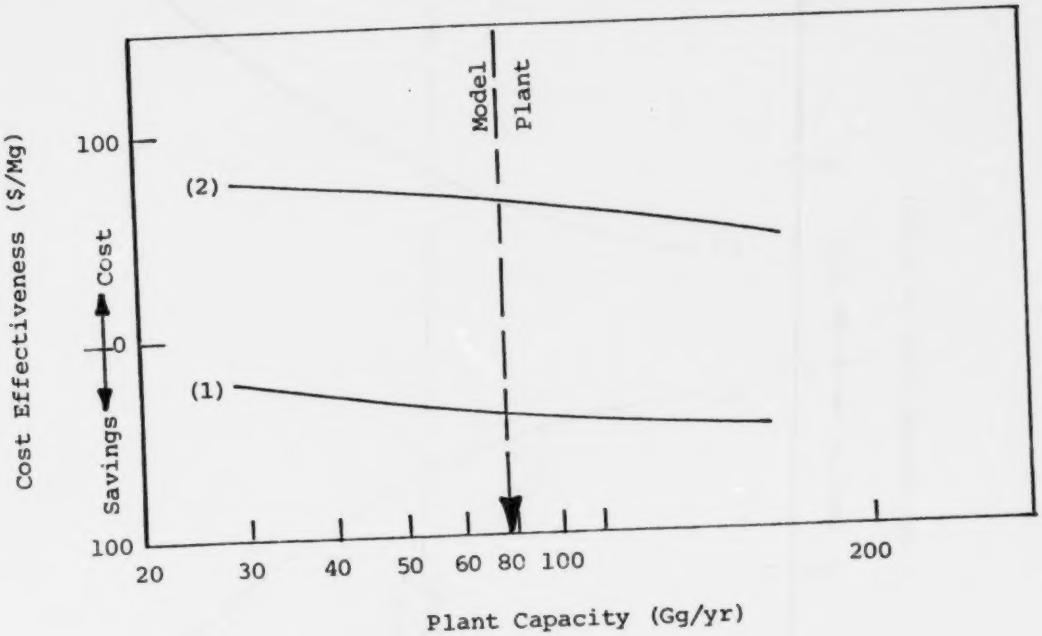
(1) Liquid-fume thermal oxidizer with heat recovery.
(2) Liquid-fume thermal oxidizer without heat recovery.

Fig. VI-1. Installed Capital Cost vs. Plant Capacity for Integrated Model Plant Emission Controls



(1) Liquid-fume thermal oxidizer with heat recovery.
(2) Liquid-fume thermal oxidizer without heat recovery.

Fig. VI-2. Net Annual Cost vs. Plant Capacity - Liquid-Fume Thermal Oxidation



(1) Liquid-fume thermal oxidizer with heat recovery
(2) Liquid-fume thermal oxidizer without heat recovery.

Fig. VI-3. Cost Effectiveness vs. Plant Capacity for Integrated Model Plant Emission Controls

Table VI-2. Emission Control Cost Estimates and Cost Effectiveness for Integrated Acrylic Acid and Ester Model Plant

Emissions Sources	Control Device or Technique	Total Installed Capital Cost	Annual Operating Costs			(B) Emission Deduction		(C) Total VOC Cost Effectiveness (per Mg)
			Gross Annual[a]	Recovery Credit	(A) Net Annual	Total VOC (Mg/yr)	(%)	
b	Thermal oxidizer, no heat recovery	$ 830,000	$491,000		$ 491,000	7,748	99	$63
b	Thermal oxidizer, waste-heat boiler	1,270,000	643,000	$936,000	(293,000)[c]	7,748	99	(38)[c]

[a] Includes credit for liquid waste heat value.

[b] Includes quench-absorber off-gas, all combined vents, working storage vents, 50% of fugitive sources, all handling vents and liquid organic wastes.

[c] Savings.

model plant. The process for performing the acid recovery can be of three types: regeneration through the oxidation of sulfur compounds, vacuum concentration, and atmospheric concentration. Organics entering these processes with the spent acid accumulate as carbonaceous material in the equipment, are oxidized to CO or CO_2, leave with the aqueous waste streams, or leave with the uncondensed gases as VOC emissions. Distribution of the organics entering the different processes for acid recovery may be expected to vary considerably. Control technology for VOC reduction includes reduction of organics entering the equipment, optimizing the combustion of organics to CO or CO_2, and gas scrubbing or other technologies to remove VOC from the waste gases. Cost evaluation of these control methods is highly site-specific and dependent on the acrylic ester process chemistry. Cost evaluation is not included in this report. No control is specified at this time. Control of emissions from sulfuric acid recovery processes will be handled as a separate product report.

4. Uncollected Fugitive Sources

Control technology for uncollected (not included in the suction manifold system) fugitive emission sources will be discussed in a future EPA document.

5. Other Processes

The high-pressure modified Reppe process for acrylic acid uses a flare to burn CO and acetylene waste gases from the reaction equipment. The wide use of a volatile solvent in the process requires condensers for solvent recovery.

The esterification section associated with the high-pressure modified Reppe process uses condensers and a water scrubber to control organic emissions. The water scrubber operates on all the noncondensable gases passing through the vacuum systems required for processing. VOC reduction efficiency for this unit is reported to be 95%.[3]

B. ENVIRONMENTAL AND ENERGY IMPACTS

Table V-1 reflects the environmental impact of reducing VOC emissions by application of the described control systems to the model plant.

2. Floating-Roof Storage

Storage emission control through the use of floating-roof tanks does not consume energy and has no adverse environmental or energy impacts.

C. REFERENCES*

1. J. W. Blackburn, IT Enviroscience, Control Device Evaluation. Thermal Oxidation (July 1980) (EPA/ESED report, Research Triangle Park, NC).

2. D. G. Erikson, IT Enviroscience, Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

3. Nonconfidential information received May 1978 from Dow Badische Co., Freeport, TX (on file at EPA, ESED, Research Triangle Park, NC).

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*Usually when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

Acrylic acid and its esters are produced in integrated plants using propylene oxidation for the acrylic acid and direct esterfication for the lower and heavy esters. The low-pressure modified Reppe process produces the lower acrylic esters directly but is being phased out in favor of a new propylene oxidation/direct esterification plant. One manufacturer continues to use the high-pressure modified Reppe process for acrylic acid but has announced plans to replace it in the early 1980s with a planned propylene oxidation plant. Total present acrylates capacity is reported to be 618.4 Gg/yr.

The annual growth of acrylic acid is estimated to range from 9.5 to 11.3%, and the growth of the acrylate esters is expected to range from 7.1 to 8.4%. New capacity has been announced for startup in the early 1980s.

Tables IV-14 and V-1 list the uncontrolled and controlled emission levels, respectively, for the model plant. The sizing of the model plant was based upon the relative consumption of acrylic acid to produce EA, BA, and 2-EHA and should represent a typical acrylate facility from an emissions standpoint. Total nationwide uncontrolled emissions for the industry are estimated at 5200 kg/hr, and considering the present level of control, current national emissions are 520 kg/hr. This is based on an estimated 90% control at existing plants. The acrylic acid and ester industry practice a high level of organic emission control since the chemicals they handle possess significant odor and toxic properties.

The major control device is a liquid-fume thermal oxidizer. If heat recovery is included, this unit generates significant net levels of energy from waste combustion. The model plant achieves VOC reduction efficiencies of 99% if the liquid organic wastes are included in the calculation. Efficiencies of 97.8% are achieved if only fumes are considered.

Control of storage losses by use of floating-roof tanks have lower reduction efficiencies and relatively poor cost effectiveness. Combustion of these storage emissions is an alternative control technique for storage emission control.

APPENDIX A

Table A-1. Physical Properties of Acrylic Acid, Ethyl Acrylate, Butyl Acrylate, 2-Ethylhexyl Acrylate, Ethanol, n-Butanol, and 2-Ethylhexanol

	Physical Properties									
				Vapor Pressure Coefficients[b]						
Organic	Molecular Formula	Molecular Weight	Physical State[a]	Antoine A	Antoine B	Antoine C	Boiling Point (°C/kPa)	Vapor Specific Gravity[c]	Liquid Density (g/ml)	Water Solubility (mg/liter)[c]
Acrylic acid[d]	$C_3H_4O_2$	72	Liquid	16.5617	3319.18	-80.15	141/101[e]	2.50	1.045[e] (25/4°C)	Miscible
Ethyl acrylate	$C_5H_8O_2$	100	Liquid	16.0890	2974.94	-58.15	43/13.7[e]	3.50	0.9234[e] (20/4°C)	20,000
Butyl acrylate	$C_7H_{12}O_2$	128	Liquid			23.06[f]	35/1.1[e]	4.42	0.8998[e] (20/4°C)	1,600
2-Ethylhexyl acrylate	$C_{11}H_{20}O_2$	184	Liquid			1.97[f]	85/1.07[e]	6.35	0.8852[e] (20/4°C)	~100[e]
Ethanol	C_6H_6O	46	Liquid	18.9119	3803.98	-41.68	78.4/101[c]	1.60	0.789[c] (20/4°C)	Miscible
n-Butanol	$C_4H_{10}O$	74	Liquid	17.2160	3137.02	-94.43	117.7/101[c]	2.55	0.810[c] (20/4°C)	77,000
2-Ethylhexanol	$C_8H_{18}O$	130	Liquid	15.3614	2773.46	-140.0	183.5/101[c]	4.49	0.834[c] (20/20°C)	1,000

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[a] As monomer.

[b] Antoine equation: ln (vapor pressure in mm Hg) = A - [B/(T + C)], where T is temperature in Kelvin; references: R. C. Reid, J. M. Prausnitz, T. K. Sherwood, The Properties of Liquids, 3d ed., McGraw-Hill, New York, 1977.

[c] K. Verschueren, Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold, New York, 1977.

[d] Melting point of acrylic acid is 13.5°C.

[e] J. W. Nemec and W. Bauer, Jr., "Acrylic Acid and Derivatives," pp. 330-354 in Kirk-Othmer Encylcopedia of Chemical Technology, 3d ed., Wiley, New York, 1978.

[f] Actual vapor pressures, kPa at 100°C; from footnote e.

Table B-1. Air-Dispersion Parameters

	Number of Sources	VOC Emission Rate (g/sec)	Tank Height (m)	Tank Diameter (m)	Stack Height (m)	Stack Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
I. Model plant (uncontrolled)									
A. Processing Unit 1									
1A	1	227			15	0.82	293	7.98	15.2
1B, 1C	2	0.28[a]			15	0.15	293	0.25	15.2
1D, 1E, 1F, 1G	4	7.20[a]			15	0.048	293	0.028	15.2
1H	b	0.120[a]					b		
B. Processing Unit 2									
3H, 4H, 5H		0.018[a]					293		
C. Processing Unit 3									
3A, 3B, 3C	3	0.67[a]			15	0.032	293	0.012	15.2
3D, 3E, 3F	3	4.68[a]			15	0.083	293	0.083	15.2
3H	b	0.241[a]					b		
D. Processing Unit 4									
4A, 4B, 4C	3	0.075[a]			15	0.012	293	0.002	15.2
4D, 4E, 4F	3	0.531[a]			15	0.031	293	0.012	15.2
4H	b	0.116[a]					b		
E. Processing Unit 5									
5A, 5B	2	1.01[a]			15	0.020	293	0.005	15.2
5C, 5D, 5E	3	0.525[a]			15	0.019	293	0.004	15.2
5H	b	0.001[a]					b		
F. Processing Unit 6									
1. AA hypothetical solvent tank	1	0.143	12.19	10.13					
2. AA tank	4	0.007[a]	7.31	4.74					
3. EA-BA hypothetical solvent tank	1	2.108	12.19	29.84					
4. Ethanol tank	1	0.117	12.19	21.43					
5. EA tank	1	0.431	12.19	26.93					
6. Butanol tank	1	0.025	12.19	17.47					
7. BA tank	1	0.075	12.19	20.12					
8. 2-EHA hypothetical solvent tank	1	0.017	2.44	1.67					
9. 2-Ethylhexanol	1	0.001	12.19	12.94					
10. 2-EHA	3	0.001[a]	9.75	7.26					
G. Processing Unit 7									
Loading losses									
Drum loading	1	0.014			10	0.051	Ambient		
Tank car/tank truck	1	.0.008			3	0.051	Ambient		
Barge	1	0.041			3	0.051	Ambient		
H. Secondary									
Waste-water treatment	1	0.101	1	320			Ambient		
Solid organic wastes	1	0.033			10	1	533		
Sulfuric acid recovery	1	11.61			15	1	353		
II. Model plant (controlled)									
A. Liquid-fume thermal oxidizer flue gas	1	5.47			15	1.15	533	15.9	15.2
B. Processing Unit 6[d]									
1. AA hypothetical solvent tank	1	0.022	12.19	10.13					
2. EA-BA hypothetical solvent tank	1	0.316	12.19	29.84					
3. Ethanol tank	1	0.018	12.19	21.43					
4. EA tank	1	0.065	12.19	26.93					

[a] All sources.

[b] See Table IV-1.

[c] Other tank emissions are uncontrolled.

APPENDIX C

FUGITIVE EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore, the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below:

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

COST ESTIMATE SAMPLE CALCULATIONS

A. COST ESTIMATE DETAILS

This appendix contains sample calculations showing how the costs presented in this report were estimated.

The accuracy of an estimate is a function of the degree of data available when the estimate was made. Figure D-1 illustrates this relationship. The contingency allowance indicated is included in the estimated costs to cover the undefined scope of the project.

Capital costs given in this report are based on a screening study, as indicated by Fig. D-1, based on general design criteria, block flowsheets, approximate material balances, and data on general equipment requirements. These costs have an accuracy range of +30% to -23%, depending on the reliability of the data, and provide an acceptable basis to determine the most cost-effective alternative within the limits of accuracy indicated.

B. THERMAL-OXIDIZER-CONTROLLING INTEGRATED PLANT EMISSIONS

The emissions from the integrated acrylic acid and ester model plant were estimated to be 17,200 scfm with a heat content (including CO level) of just under 47 Btu/scf. A heat content of 50 Btu/scf was therefore assumed. Since the emissions contained over 2 vol% CO, the following combustion conditions were chosen. The combustion temperature was 1600°F, and the residue time was 0.75 sec. Figure V-4 in the Control Device Evaluation. Thermal Oxidation report[1] was used to estimate the capital costs of the thermal oxidizer with no heat recovery and the thermal oxidizer using a 250-psi steam waste-heat boiler. Then annual costs were developed by using the table on p. B-22 of Appendix B in the cited report.[1] Annual costs were developed for the model plant as shown in the following calculation for the heat recovery case:

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[1] J. W. Blackburn, IT Enviroscience, Control Device Evaluation. Thermal Oxidation (July 1980) (EPA/ESED report, Research Triangle Park, NC).

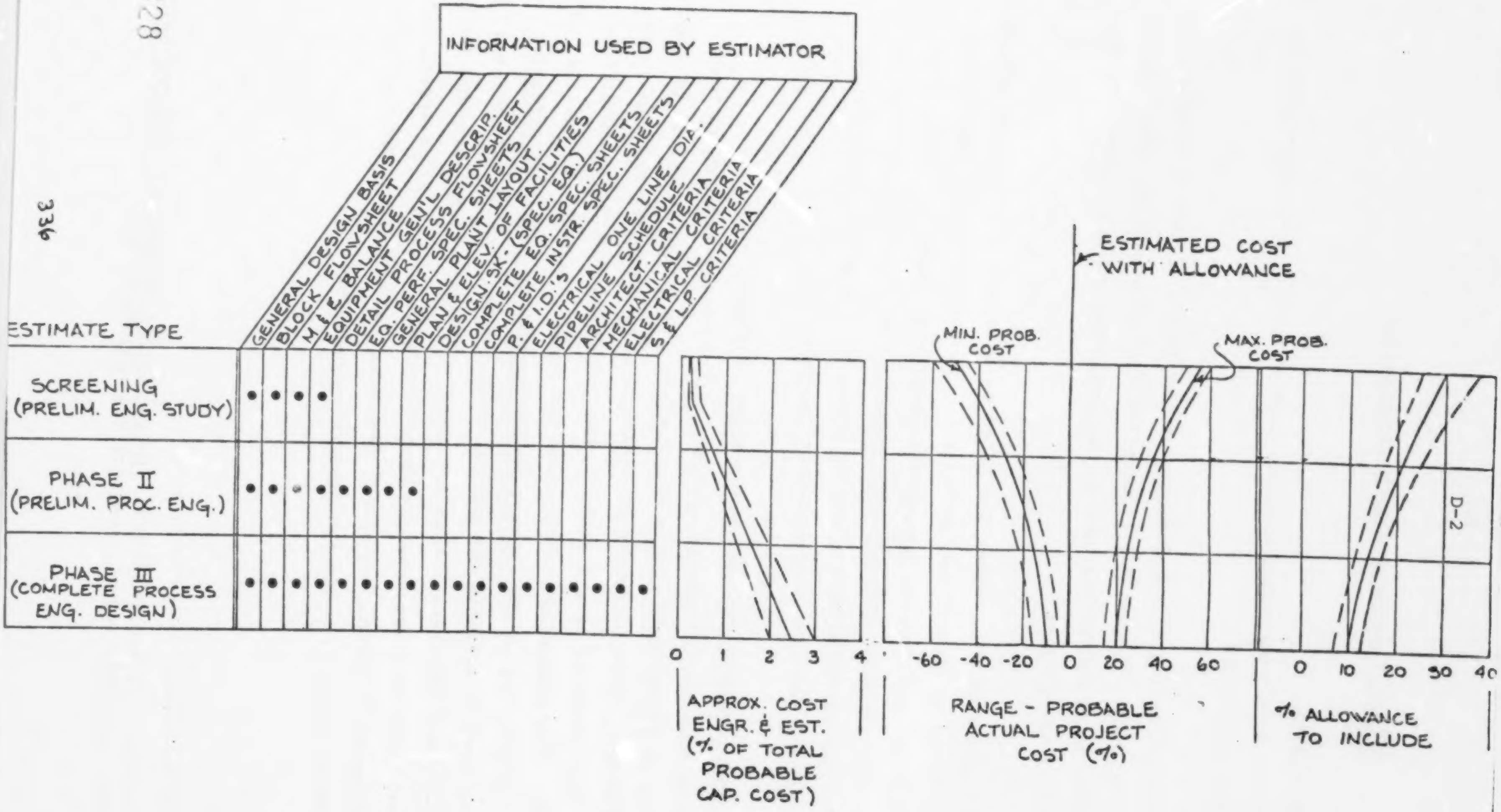

Fig. D-1. Precision of Capital Cost Estimates

LATEST REVISION - 5/2/77

Fixed Costs: $1,270,000 x 0.29 = $368,000

Utilities: $\frac{17{,}200\ \text{scfm}}{5{,}000\ \text{scfm}} \times \$169{,}000$ = $581,000

Manpower: = $ 36,000

Recovery Credit: $\frac{17{,}200\ \text{scfm}}{5{,}000\ \text{scfm}} \times \$272{,}000$ = $936,000

In addition, there is a fuel credit for burning waste organic liquids in the thermal oxidizer. It is estimated that the heat value of this source is 19.5 M Btu/hr. At $2.00/million Btu, then, this lowers the utility cost by $342,000 annually. The net annual savings therefore are as follows:

Fixed costs	$368,000
Utilities	239,000
Manpower	36,000
Recovery credit	-936,000
	-$293,000

From Table VI-2 of this report:

Emission reduction = 7748 Mg of VOC/yr

Cost effectiveness = $\frac{-293{,}000}{7748}$ = $38 saved/Mg of VOC

EXISTING PLANT CONSIDERATIONS

I. EXISTING PLANT CHARACTERIZATION

Table E-1 lists emission control devices reported to be in use by industry. To gather information for this report two site visits were made to acrylic acid and esters manufacturers. Trip reports have been cleared by the companies concerned and are on file at EPA, ESED, in Durham, NC.[1,2] EPA also has received letters in response to requests for information on air emissions from acrylic acid and esters plants. Some of the pertinent information concerning process emissions from existing acrylic and acid esters facilities is presented in this appendix.

A. UNION CARBIDE - TAFT, LA

The capacities for the UCC acrylates facilities are about 200 million lb/yr of acrolein, acrylic acid, and esters. Acrylic acid comprises 130 million lb/yr of this total. Ethyl acrylate capacity is 90 million lb/yr. Total heavy ester capacities (such as 2-ethylhexyl acrylate) are 110 million lb/yr. UCC considers butyl acrylate to be a heavy ester.

The facility was originally built in 1969 and utilized British Petroleum technology for acrylic acid production. In 1976 the plant was converted to technology obtained under license from SOHIO.

1. Acrylic Acid

a. Process Emissions -- The various process emissions are described below:

Quench absorber and acrolein distillation off-gas -- The off-gas stream containing unreacted oxygen, nitrogen, and organics is combined with emissions from the acrolein distillation and routed to a thermal oxidizer that UCC calls a "combuster" or "buster." Vent streams from the acrolein process also are sent to this device, as is the feed. Sampled data do not exist, but have been calculated based on reliable UCC pilot studies. The predicted design loading on the combuster before its installation in 1975 was 4835 lb/hr of volatile organic compounds (VOC), not including methane. A conservative estimate of the

Table E-1. Control Devices Currently Used by the Domestic Acrylic Acid and Esters Industry

	Emission Points										
				Storage				Secondary			
Company	Quench-Absorber Off-Gas	Atmospheric Equipment Vents	Vacuum Equipment Vents	Working	Tank Farm	Fugitive	Handling-Loading	Wastewater	Liquid Organic Residues	Solid Organic Residues	Sulfuric Acid Recovery
Celanese Clear Lake, TX	Thermal oxidizer	Thermal oxidizer	Thermal oxidizer	Thermal oxidizer	Thermal oxidizer	Thermal oxidizer	Thermal oxidizer	Thermal oxidizer	Thermal oxidizer	Solids incinerator	N.D.[a]
Pampa, TX	b	N.D.	N.D.	N.D.	Collected and flared	N.D.	Vapor recovery	N.D.	N.D.	N.D.	N.D.
Dow Badische Freeport, TX	c	Flares, condensers, scrubbers			Vapor scrubbers[d]	N.D.	Vapor recovery	N.D.	Incinerator	N.D.	N.D.
Rohm and Haas Deer Park, TX	Thermal oxidizer	Thermal oxidizer	Thermal oxidizer	Thermal oxidizer	Thermal oxidizer[e]	Thermal oxidizer	Dedicated fume incinerator	Thermal oxidizer[e]	Thermal oxidizer	Landfill	None
Union Carbide Taft, LA	Thermal oxidizer	Flare[e]	Flare[e]	Floating roof, blanketing gas, vapor recovery, conservation vents, flare		None	Dedicated catalytic incinerator	None	Thermal	Solids incinerator	N.D.

[a] N.D. = No data.

[b] Acrylic acid not manufactured.

[c] Propylene oxidation not used.

[d] Used on some tetrahydrofuran and acrylic acid tanks. Most tanks have no control.

[e] Some fumes only.

resulting flue gas from this device yields the following organic emissions based on capacity operation: VOC, 37 lb/hr; CO, 64 lb/hr; and NO_x, 60 lb/hr. UCC personnel estimate that two-thirds of this organic loading is attributable to acrylic acid production and that the rest results from acrolein production. This stream will vary directly with the production rate.

Feed to flare (including raffinate stripper vent -- This is a continuous stream comprising the primary feed to a flare. Acrolein process vents and extraction system vents are also included. The total flow rate of this stream is 60,000 lb/day, and an estimate of the composition is shown below. This stream will vary independently with production rate since it is largely made of nitrogen blankets or purges.

Component	Amount (wt %)
VOC	0.006
CO_2	18.59
N_2	81.11
CO	0.25
CH_4	0.002

Extract distillation vent -- Several vents from vacuum distillation equipment are combined as this stream. Nitrogen is bled into this equipment to prevent oxidation and to control vacuum. A makeshift water scrubber (old piece of pipe) has been installed on the stream and the off-gas from the scrubber has been measured. The temperature of the stream is 113°F, and the flow rate is 0.011 lb of gas/lb of acrylic acid produced at capacity. Acrylic acid capacity is 130 million lb/yr. This emission rate varies independently with plant production since the stream is vented from vacuum equipment. The composition of the stream is given below:

Component	Amount (wt %)
Hydrocarbon solvent	34.15
Acrylic acid	0.03
CO_2	1.19
O_2	1.12
N_2	63.51

Foreruns distillation vent -- Acetic acid is distilled in several vacuum stills, where nitrogen is added to control vacuum and to prevent oxidation. The measured flow rate for this stream is 0.0073 lb of gas/lb of acrylic acid produced at capacity. This emission varies independently with production since the stream is vented from vacuum equipment. The composition data are given below:

Component	Amount (wt %)
Hydrocarbon solvent	9.64
Acrylic acid	0.03
O_2	0.88
N_2	89.31
H_2O	0.14

Acrylic acid distillation vent -- Acrylic acid is distilled in vacuum equipment into which nitrogen is bled to control vacuum and to prevent oxidation. The measured flow rate is 0.0040 lb of gas/lb of acrylic acid produced at capacity. This emission varies independently with production since the stream is vented from vacuum equipment. Its composition is given below:

Component	Amount (wt %)
Hydrocarbon solvent	0.84
CO_2	0.16
O_2	3.45
H_2O	0.68
N_2	94.87

Shutdown related emissions -- The acrylic acid process requires shutdown at varying intervals from 4 to 12 times a year. Organics are flushed from the system and are then recovered. Nitrogen is introduced during filling and emptying procedures. When vacuum equipment is placed under vacuum, UCC personnel anticipate no VOC in the vented nitrogen.

b. Secondary Emissions -- Two secondary emission sources result in acrylic acid manufacture. The first is the polymeric residues removed periodically from the stills and equipment. Generation of this polymer is undesirable, and much care is taken to prevent it. Still, up to 50 fiberpacks a year of material are estimated to be removed from the equipment by hand and burned in an incinerator. UCC assumes complete combustion.

The second emission is a result of heat transfer equipment at Taft. The emissions from the two vents involved are shown below. The flow from vent 1 is 0.00045 lb of VOC per pound of AA produced; the flow from vent 2 is not given.

	Amount (wt %)	
Component	Vent 1	Vent 2
VOC	31.0	None
H_2O	54.0	None
N_2	15.0	75.17
CO	None	0.12
CO_2	None	3.22
CH_4	None	0.01
O_2	None	21.48

c. Fugitive Emissions -- Much of the equipment in this process is under vacuum. Therefore emissions from seals may be much lower than those from systems at or above atmospheric pressure. All but ten pumps are on vacuum service. Pumps in this equipment can still be under positive pressure even though the equipment is under vacuum.

The amount of cooling water used for acrylic acid and acrylates production is shown below:

	Amount (M gal/day)
Acrylic acid	54.4
Ethyl acrylate	8.7
Heavy acrylate	5.8

The following discussion is taken from a packet submitted to EPA by UCC on March 17, 1978.

> "Organic contamination in the cooling water system is detected by total carbon analysis. These analyses are performed daily on 24-hour composited samples of cooling water entering and leaving a process unit. If the outlet total carbon concentration exceeds the inlet, additional cooling water samples are taken from within the unit and analyzed to determine the source of contamination. The necessary corrective action is then taken to eliminate the source of contamination."

Wastewater generated in acrylic acid and ester production is sent by closed pipe to a primary treatment plant (including oil skimming), then to an equalization pond, and finally to a UNOX waste treatment plant.

d. Handling Emissions -- Acrylic acid and esters are handled by drumming, tank car loading, and tank truck loading (see Table E-2).

e. Emission Control Devices -- Two major emission control devices are used in acrylic acid and acrylate ester manufacture: thermal oxidizers and flares.

Thermal oxidizer (combuster) -- A thermal oxidizer or combuster was installed in 1975 to destroy acrylic acid and acrolein vapors. This unit was constructed by John Zinc and incorporates a heat recovery unit to produce process steam at 600 psig. When or if the combuster goes down, the acrylic acid plant also goes down.

Table E-2. Control Devices - Product Handling

	Air Emission Control Equipment	
	Acrylic Acid	Acrylates
Drumming	Catalytic oxidation[a]	None[b]
Tank car loading	Submerged fill pipe	Scrubbing[c] (99% eff.)
Tank truck loading	Submerged fill pipe	Scrubbing[c] (99% eff.)

[a] Approximately 10% of the acrylic acid is drummed at the No. 2 Drumming Building, which utilizes catalytic oxidation to destroy organic vapors coming from the operation. Approximately 90% of the acrylic acid is drummed at the No. 3 Drumming Building, which is equipped with vent hoods to remove organic vapors from the work place. The hoods are vented to the atmosphere.

[b] Acrylate vapors are not scrubbed at the drumming facilities but are pulled up through vent hoods to remove them from the work place. The hoods are vented to the atmosphere.

[c] Contaminated water, spills, and hose and pipeline washings are collected in a chemical sump at each loading facility. The collected wastes are pumped to a waste treatment plant that has primary and secondary waste-treatment facilities.

The unit operates at a relatively constant feed input and supplements the varying flow and fuel value of the streams fed to it with inversely varying amounts of fuel gas. Fuel-gas consumption averages 52.8 million Btu/hr instead of the designed level of 36 to 51 million Btu/hr. The unit is run with 9% excess oxygen instead of the designed 3 to 5% excess oxygen.

The propylene used in the acrylic acid oxidation contains about 2% propane, which acts as an inert gas in the acrylic acid process and enters the incinerator in the waste gas. With the planned startup of a new olefins plant the propane concentration in the propylene should double to 4%, thus achieving an oxidation feed of 4% propane and therefore the conditions for which the combuster was designed.

Materials of construction of a nonreturn block valve in the 600-psig steam line from the boiler section requires that the incinerator be operated at 650°C instead of the designed 980°C. Residence time is 3 to 4 sec.

The capital cost of this unit was $3 million in 1976. Operating costs excluding capital depreciation are reported to be $287,000/year (1976).

Flare -- Before the combuster was installed, the acrolein-containing streams were routed to a flare. This unit still operates on streams from acrolein production and acrylic acid production. Acrolein streams routed to the flare include the acrolein distillation column, the acrolein unit tanks, and discharges from the acrolein unit safety valves. Acrylic acid streams vented to the flare include the acrylic acid extractor vent, the raffinate stripping column vent, and the field acrolein tank safety-valve discharges. The vent header from the acrolein production area can be routed to the combuster. However, the other header from the acrylic acid area can be routed only to the flare.

2. Ethyl Acrylate

a. Process Emissions -- The three major process-related emissions involved in the production of ethyl acrylate are described below:

Ester extraction vents -- The flow rate for this stream is 0.012 lb of gas/lb of ethyl acrylate produced, and the annual ethyl acrylate capacity is 90 million lb/year. The measured composition of the stream is as follows:

Component	Amount (wt %)
Denaturant	0.19
Ethyl acrylate	2.43
Ethyl ether	0.20
Ethanol	1.7
O_2	13.0
N_2	79.57
H_2O	1.09
CH_4	1.82

Ester refining vents -- This stream is the discharge from vacuum systems supplying vacuum to the refining equipment. The flow rate is 0.083 lb of gas/lb of ethyl acrylate produced. The composition is shown below:

Component	Amount (wt %)
Ethyl acrylate	0.74
Denaturant	1.55
Ethyl ether	2.02
Ethanol	0.18
O_2	2.94
N_2	91.65
H_2O	0.92

b. Shutdown-Related Emissions -- This system requires shutdown from 12 to 24 times a year. Nitrogen is introduced to the equipment during emptying and filling, and care is taken to prevent the emission of organics to the sewer or air. This system does not require as much polymer cleanout as acrylic acid equipment. Cleanout is normally done in preparation for idle standby.

c. Secondary Emissions -- Secondary emissions are generated by incineration of about three fiberpacks of polymer a year and of the wastewater from the extraction and refining steps. About 12 times a year 20,000 lb of water soluble organic is wasted. Most is incinerated but some is sent to wastewater treatment. Other wastewater is sent to the wastewater treatment facilities described in Sect. I-A.1.c.

d. Fugitive Emissions -- The data on pumps, valves, and seals are discussed in Sect. E-I.A.1.c. Cooling water usage is shown in Sect. E-I.A.1.c.

e. Handling Emissions -- Handling emissions are discussed in Sect. E-I.A.1.d; data on control devices are given in Table E-2.

f. Control Devices -- The process vents described for ester production emit directly to the atmosphere.

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3. Heavy Ester

a. Process Emissions -- Heavy-ester production includes butyl and 2-ethylhexyl acrylates. About 110 million lb of heavy esters are produced annually at capacity. Data on the two sources of process emissions -- reactor vents and refining vents -- are given below:

Reactor vents -- The flow of the stream leaving the reactors is 0.029 lb of gas/lb of heavy ester produced. The composition is as follows:

Component	Amount (wt %)
Hydrocarbon solvents	13.96
Ethyl ether	1.60
Light boiler	1.28
CO_2	0.14
Ar	0.26
O_2	6.40
N_2	75.78
H_2O	0.47
CH_4	0.11

Refining vents -- The flow of this stream is 0.0128 lb of gas/lb of heavy ester produced, and the composition is the following:

Component	Amount (wt %)
Several light-organic unknowns	9.74
Ar	0.61
O_2	11.56
N_2	77.48
H_2O	0.61

b. Secondary Emissions -- Aqueous wastes and incinerable residues are generated in this process.

c. Fugitive Emissions -- Data on fugitive emissions are the same as those given in Sect. E-I.A.1.c. The amount of cooling water used is also given in that section.

d. Handling Emissions -- Handling emissions are discussed in Sect. E-I.A.1.d. Data on control devices are given in Table E-2.

e. Control Devices -- Process vents emit directly to the atmosphere.

B. ROHM AND HAAS - DEER PARK, TX

Acrylic esters are produced from propylene, air, and alcohols, with acrylic acid being produced as an intermediate. Acrylic acid is produced directly from propylene by a vapor-phase catalytic air-oxidation process. The reactions take place in two steps, both in the presence of steam as a diluent. Propylene is first oxidized to acrolein, which is then oxidized to acrylic acid.

A small amount of acetic acid is produced as a by-product. The reactions take place in fixed-bed multitubed reactors that operate at high temperatures and atmospheric pressure. The heat of reaction is removed through indirect heat exchangers, with a cooling medium in the shell side of the reactors. This heat is then converted to steam in a boiler. There are two trains for the reaction step. Reactor effluent gas is sent to absorbers, where acrylic acid is recovered in an aqueous solution. The acrylic acid is then extracted from the aqueous stream in an extraction system common to both trains. Acrylic acid suitable for esterification with the desired alcohol is available after solvent recovery. Butyl, ethyl, and methyl esters are produced in a liquid-phase reaction using a catalyst. The reaction product is purified in subsequent refining operations. Excess alcohol is recovered and heavy-end by-products are incinerated.

Five emission sources are generated in this process. The first actually consists of two separate, closely grouped stacks having the same effluent composition. There is one stack for each of two startup heaters, each sized to produce about the same gas exit velocity. These heaters are used to heat the reactor cooling medium for startup and maintain coolant temperatures during temporary shutdowns. The normal period for continuous startup-heater operation is about three days, and startups may occur several times per year. Shutdowns of a reaction train during normal operation may occur as often as once or twice a week for as long as a few hours or up to a day. The fuel source will be natural gas. Enough air will be added to produce 6 vol % O_2 in the stack effluent. Complete combustion is assumed, with the only pollutant being NO_x. The nominal stack height and diameter have been selected that will produce the ground level concentration (GLC) for NO. The threshold limit value (TLV) for NO is 25 ppm.

The second emission point is the waste incinerator stack. The waste incinerator is designed to burn the off-gas from the two absorbers. In addition all process vents (from extractors, vent condensers, and tanks) that might be a potential source of gaseous emissions will be collected in a suction vent system and will normally be sent to the incinerator. An organic liquid stream generated in the process will also be burned, thereby providing part of the fuel requirement. A separate natural-gas line will supply the remainder. Air will be added to an amount to produce about 6% O_2 in the effluent. NO_x and a very small quantity of unburned hydrocarbon (1.75 lb/hr) are the only anticipated contaminants.

The third emission point is the suction vent gas (SVG) flare, which will be used only to incinerate the collected suction vent gases during waste incinerator maintenance shutdowns and during severe process upsets. NO_x is the only anticipated contaminant, as the flare will be of a smokeless design.

The fourth emission point is the absorber off-gas (AOG) flare. This will also be used only when the incinerator is shut down for maintenance. The only anticipated contaminant is NO_x.

The fifth emission source consists of the vents from five storage tanks.

Table E-3 summarizes emission information given by Rohm and Haas.

C. CELANESE -- CLEAR LAKE, TX

The Clear Lake Plant of Celanese supplied the information given in Tables E-4, E-5, and E-6 in response to an EPA information request.[3]

Table E-3. Emission Data from Rohm and Haas

Emission Source	Emission Rate (lb/hr)	
	VOC	NO_x
Startup heaters		25
Waste incineration stack		50
Suction vent gas flare	2.02	
Absorber off-gas flare	None	Some; quantity not reported
Storage tank		47

Table E-4. Acrylic Acid/Acrylate Ester Emission Factors

Component	Acrylic Acid Plant[a] (lb/1000 lb of Acrylic Acid)		Ethyl Acrylate Combined Processing[b] (lb/1000 lb of Ethyl Acrylate)	Butyl Acrylate Combined Processing[b] (lb/1000 lb of Butyl Acrylate)
	Quench Absorber Off-Gas	Combined Processing		
Acetaldehyde	<0.1			
Acetic acid	1.4			
Acetone	1.3			
Acrolein	4.5			
Acrylic acid	18.0			
Ethyl acrylate	1.2	0.9		
Butyl acrylate				0.4
Butanol				0.4
Water	88.6	0.1		1.9
Carbon dioxide	269.5		2.1	
Carbon monoxide	118.5			
Nitrogen	4,466.6	29.7	10.3	
Oxygen	128.8	8.8	2.7	
Propane	75.3			
Propylene	17.5			
Air				19.2
Ethane			42.5	
Total	5,191.2	39.5	57.6	21.9

[a] Operating temperature, 80°F.

[b] Operating temperature, 120°F.

[c] Hydrocarbons calculated as ethane.

Table E-5. Composition of Other Waste-Gas Streams

	Composition (lb/hr)		
Component	Tank Farm and Handling[a]	Tank Car Wash[a]	Ventilation Feed[b]
Nitrogen	368	158	126,900
Oxygen			33,700
Acrylic acid	Unknown	Unknown	
Ethyl acrylate	Unknown	Unknown	Unknown
Butyl acrylate	Unknown	Unknown	

[a] Operating temperature, 70 to 90°F.

[b] Operating temperature, 90°F.

Table E-6. Composition of Incinerator Flue Gas

Component	Volume (mole %)
Oxygen	13.25
Carbon dioxide	2.28
Carbon monoxide	<0.001
Nitrogen	83.51
Argon	0.81
Methane	0.1350
Ethane plus	<0.001
Hydrogen sulfide	<0.0021
Sulfur dioxide	0.0150
Caronyl sulfide	<0.0017
Carbon disulfide	<0.0017
Nitrogen oxides	<0.0028

D. DOW-BADISCHE, FREEPORT, TX

The Dow-Badische process is completely different from the processes used by the other three manufacturers in that the high-pressure modified Reppe process is used to make acrylic acid and direct esterification is used to make the esters. It is planned to shut down the plant and to start up a propylene oxidation in its place in 1981.

The emissions are reported[4] to be the following. The absorber and reactor vent gas is fed to a flare, and the stream typically has a total flow of 187 lb/hr, composed of the following: CO, 164.5 lb/hr; C_2H_2, 15 lb/hr; C_2H_4, 3.0 lb/hr; N_2, 3.0 lb/hr; and CO_2, 1.5 lb/hr. The temperature is 13°C. 99% efficiency is claimed for the flare. Vacuum-jet emissions are given as 92% air and 8% water for two sources and 77% air and 23% water for the third source. The flows are 8 scfm for the first two sources and 26 scfm for the third source. A fugitive loss of 15 tons/yr of tetrahydrofuran is given. None of these emissions are controlled.

Wastewater comes from miscellaneous intermittent sources throughout the plants. Organics are primarily THF and acrylic acid, which are volatile and are disposed of through a biological treatment plant. Concentrations are 100 to 20 ppm. Organic residues are from distillation bottoms. These nonvolatile residues are incinerated on-site or are disposed of by contract.

The acrylic esters process has process emissions arising from vacuum processes. The emissions are scrubbed in a water scrubber prior to release. No organics are shown to be emitted. The flow of this stream is 1450 scfm. Storage tanks also are emission sources; however, no data are given.

Liquid wastes from the esters plant also include a distillation bottom stream, which is disposed of by incineration. Wastewater has an organic carbon concentration of 1500 to 2000 ppm (mostly butyl and 2-ethyl-hexyl acrylate) and represents about 1 lb/min of TOC.

II. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant. Because of the high level of control already exhibited by acrylic acid and ester manufacturers, it is not anticipated that retrofitting major thermal oxidizers will be necessary.

III. REFERENCES*

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2. J. W. Blackburn, IT Enviroscience, Trip Report on Site Visit to Rohm and Haas Co., Deer Park, TX, Nov. 1, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. Letter dated Apr. 21, 1978, from C. R. DeRose, Celanese Chemical Co., to Leslie Evans, EPA (on file at EPA, ESED, Research Triangle Park, NC).

4. Letter dated May 12, 1978, from R. R. Ray, III, Dow-Badisch Co., to D. R. Goodwin, EPA (on file at EPA, ESED, Research Triangle Park, NC).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 5

METHYL METHACRYLATE

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch² (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	$1\ Tg = 1 \times 10^{12}$ grams
G	giga	10^{9}	$1\ Gg = 1 \times 10^{9}$ grams
M	mega	10^{6}	$1\ Mg = 1 \times 10^{6}$ grams
k	kilo	10^{3}	$1\ km = 1 \times 10^{3}$ meters
m	milli	10^{-3}	$1\ mV = 1 \times 10^{-3}$ volt
μ	micro	10^{-6}	$1\ \mu g = 1 \times 10^{-6}$ gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Methyl methacrylate (MMA) production was selected for study because preliminary estimates indicated that total emissions of volatile organic compounds (VOC) were high and that production growth was anticipated to be high in the period between 1978 and 1982. However, as is discussed below, expansions of two plants increased the capacity of MMA beyond the present demand. Acetone cyanohydrin (ACN) is also included in this study because it is used primarily for the production of MMA. Hydrogen cyanide (HCN) is used for the production of ACN and is produced on-site; however, it is not included in this product report since it is also produced for the manufacture of other organic chemicals and will be considered as a separate organic chemical. Recent literature[1] indicates that future manufacture of MMA will be by another process (see Sect. III-D). MMA and ACN are liquids at ambient conditions. Their pertinent physical properties are given in Appendix A.

B. USAGE AND GROWTH

All the MMA produced domestically is manufactured from ACN; other products produced from ACN are methacrylic acid and its higher esters. Data on the breakdown of ACN to each of these chemicals are not available. However, one source estimates that between 1966 and 1969 only about 20% of ACN was used to manufacture methacrylic acid and its higher esters and that the remainder was used for MMA production.[2] Approximately 1 kg of ACN is required to produce 1 kg of MMA.[2]

Methyl methacrylate is used as a monomer for plastics generically referred to as acrylics. The major uses of acrylic polymers include acrylic sheet, surface coating resins, molding and extrustion powders, and emulsion polymers for adhesive, leather, paper, polish, sealant, and textile applications.[3]

Expansions occurred in 1977 that increased the current overall capacity for MMA to 511 Gg/yr. The demand for MMA for 1978 was projected to be 370 Gg/yr and is expected to increase at an average rate of 7 to 8% from 1978 to 1982. If this occurs, the production operating rate will be 84% of current capacity in 1980.[3]

C. DOMESTIC PRODUCERS

Currently there are three domestic producers manufacturing ACN and MMA at four plants: CY/RO, Du Pont, and Rohm & Haas. They all start with acetone and hydrogen cyanide to produce ACN and react the ACN with sulfuric acid and methanol to produce MMA. Table II-1 lists the MMA producers, location, and production capacities; Fig. II-1 shows the locations of the plants.

All three MMA producers have captive supplies of hydrogen cyanide and sulfuric acid. Du Pont also has captive supplies of methanol. None of the companies produce acetone.[4]

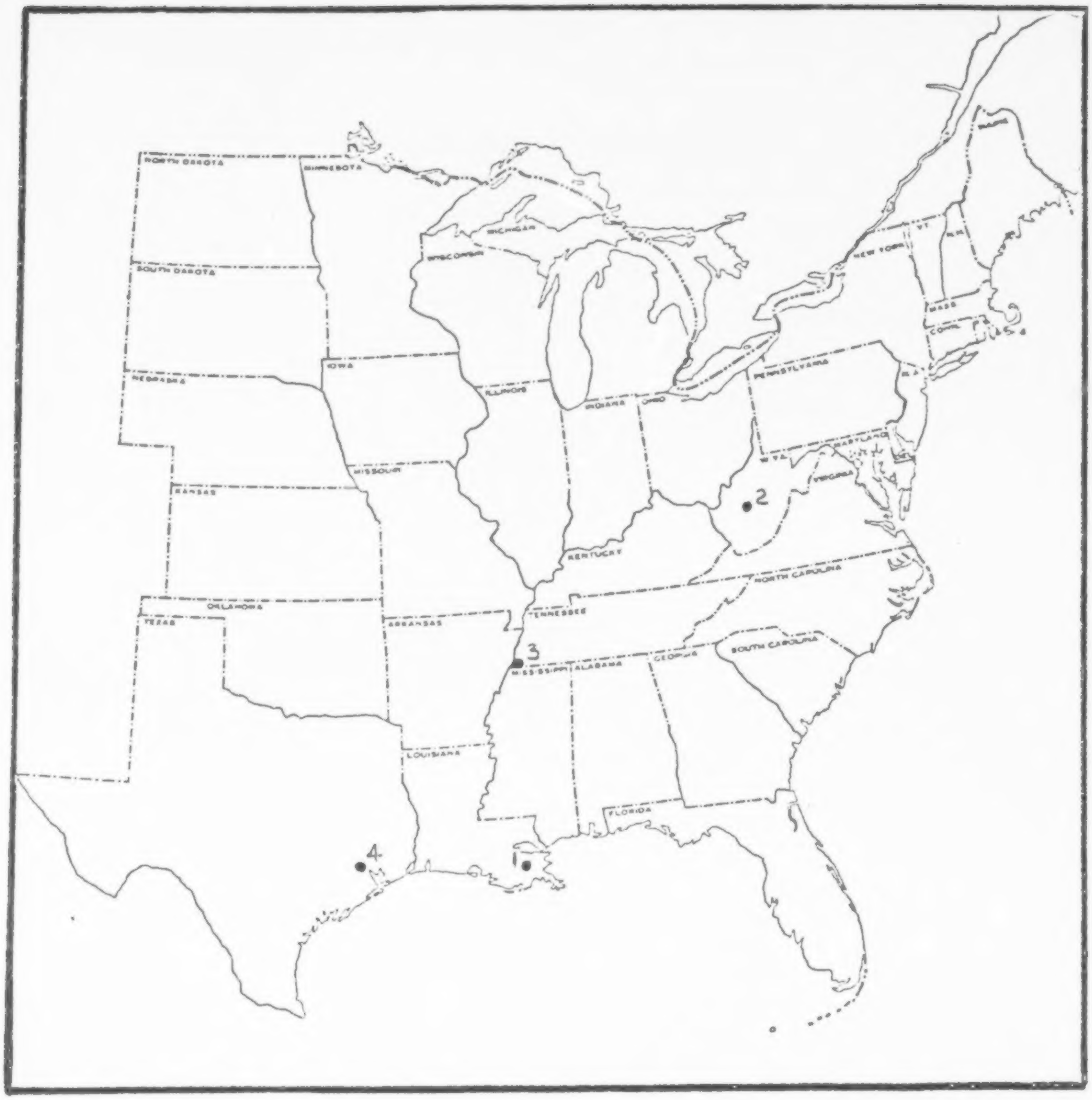
Approximately 75% of MMA production in 1975 was consumed captively. American Cyanamid (CY/RO) uses MMA captively for cast acrylic sheets and polymethacrylate molding powders. Du Pont uses MMA captively to make paints, acrylic marble, acrylic resins for surface coating, cast acrylic sheets, and polymethacrylate molding powders. Rohm & Haas uses its MMA output for cast acrylic sheets, molding powder, and other homopolymers and copolymers.[4]

Table II-1. Methyl Methacrylate Capacity[a]

Company	Location	Production Capacity (Gg/yr)[b]
CY/RO Industries	Fortier, LA	50
Du Pont	Belle, WV	61
Du Pont	Memphis, TN	100
Rohm & Haas	Deer Park, TX	300
Total		511

[a] See ref 3.

[b] As of 1979.


NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
WISCONSIN
MICHIGAN
NEW YORK
VT
N.H.
MAINE
MASS
CONN
R.I.
PENNSYLVANIA
N.J.
NEBRASKA
IOWA
ILLINOIS
INDIANA
OHIO
W.VA.
MARYLAND
VIRGINIA
KANSAS
MISSOURI
KENTUCKY
2
NORTH CAROLINA
OKLAHOMA
TENNESSEE
TEXAS
ARKANSAS
3
MISSISSIPPI
ALABAMA
GEORGIA
SOUTH CAROLINA
LOUISIANA
FLORIDA
4
1

1. CY/RO Industries, Fortier, LA
2. Du Pont Co., Bella, WV
3. Du Pont Co., Memphis, TN
4. Rohm & Haas Co., Deer Park, TX

Fig. II-1. Locations of Plants Manufacturing Methyl Methacrylate

D. REFERENCES*

1. "Big Changes in Store for Methyl Methacrylate," Chemical Engineering 85(15), 25—27 (1978).

2. J. L. Blackford, "Acetone," pp 604.5032L—604.5032M in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (January 1975).

3. J. L. Blackford, "Acetone," pp 604.5031I—604.5032L in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (July 1978).

4. J. L. Blackford, "Methyl Methacrylate," pp 674.4521A—674.4522G in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (October 1976).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

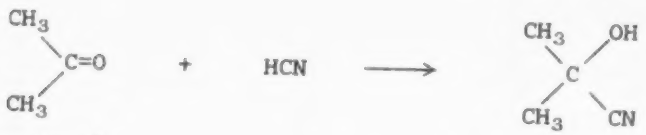
A. INTRODUCTION

All methyl methacrylate (MMA) in the United States is manufactured from ACN, which is made from acetone and hydrogen cyanide. MMA manufacturers usually purchase acetone and ship it to the plant location but manufacture the HCN on-site.

B. ACETONE CYANOHYDRIN FROM ACETONE AND HYDROGEN CYANIDE

1. Basic Process

The reactions utilized to manufacture acetone cyanohydrin are reported[1] as:



(acetone) (acetone cyanohydrin)

Figure III-1 shows a typical process flow diagram for the manufacture of ACN.[2,3] Acetone is stored in tanks before being fed to the process (Stream 1). Hydrogen cyanide (Stream 2), usually produced elsewhere at the same plant site, may be stored temporarily before being fed to the reactor. The catalyst (Stream 3), an alkali such as sodium hydroxide or other bases, is also stored. Acetone recovered later in the process (Stream 4) is combined with the other reactants in the reactor to form acetone cyanohydrin. The liquid-phase acetone cyanohydrin reaction is carried out at less than 40°C, with yields above 90% usually attained.[4] Acetone cyanohydrin readily decomposes at higher temperatures.

The sodium hydroxide in the product stream (Stream 5) is neutralized with sulfuric acid (Stream 6) to stabilize the ACN, and the solid salts formed are removed by filtration and then backwashed with water (Stream 7), which results in a salt waste stream.

The filtered crude reaction product enters a vacuum evaporation system for acetone removal (Stream 11), and the acetone cyanohydrin bottoms (Stream 10) are fed to a second evaporator. The second evaporator removes water and trace acetone (Stream 12), leaving acetone cyanohydrin product (Stream 14). The distillate (Stream 12) is

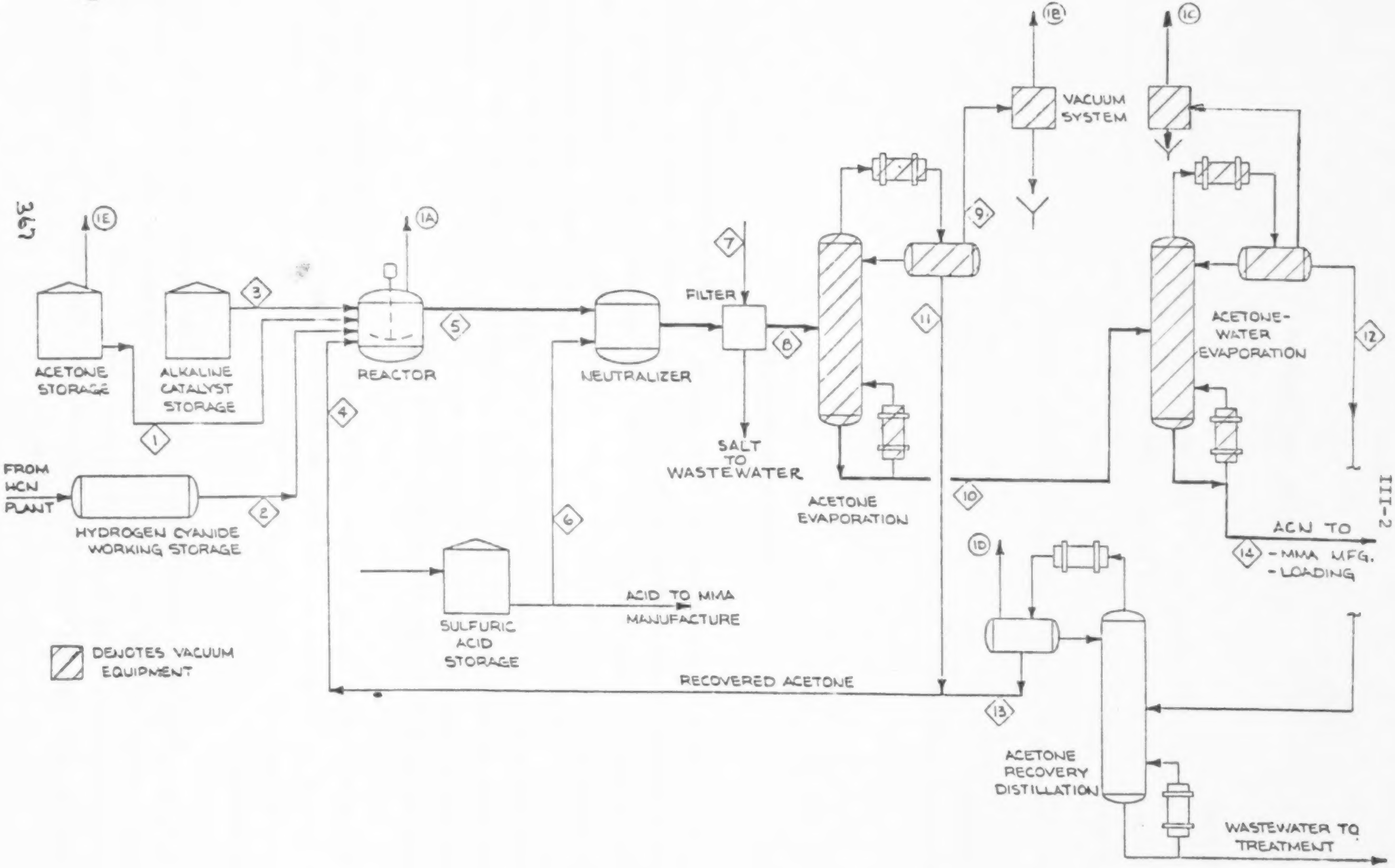

1E
ACETONE STORAGE
ALKALINE CATALYST STORAGE
1
3
FROM HCN PLANT
HYDROGEN CYANIDE WORKING STORAGE
2
1A
REACTOR
5
4
NEUTRALIZER
6
SULFURIC ACID STORAGE
ACID TO MMA MANUFACTURE
7
FILTER
8
SALT TO WASTEWATER
ACETONE EVAPORATION
9
11
10
1B
VACUUM SYSTEM
1C
ACETONE-WATER EVAPORATION
12
ACN TO
14
- MMA MFG.
- LOADING
1D
13
RECOVERED ACETONE
ACETONE RECOVERY DISTILLATION
WASTEWATER TO TREATMENT
DENOTES VACUUM EQUIPMENT

Fig. III-1. Flow Diagram for the Manufacture of Acetone Cyanohydrin

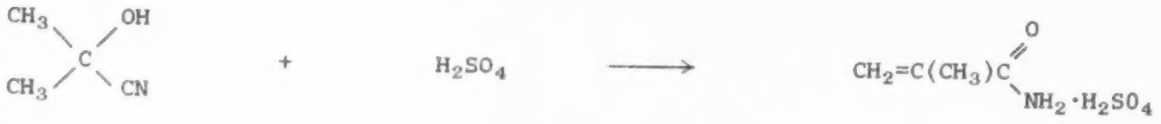
further distilled in an acetone recovery column, and the recovered acetone (Stream 13) is recycled (Stream 4) to the reactor. The aqueous bottoms from the acetone recovery column are sent to wastewater treatment.

When different catalysts are used, the solubility of the alkali sulfate salt will change, which results in various amounts of salt escaping through the filter and ultimately remaining with the acetone cyanohydrin product. The use of a salt with high solubilities in stream 8 would require subsequent distillation of ACN product to remove it from dissolved solids.

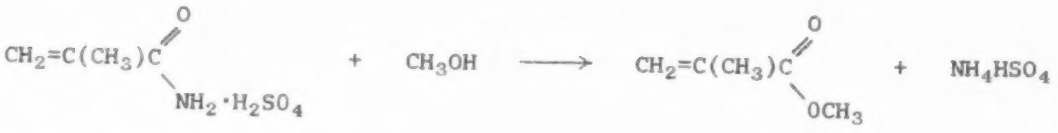
C. METHYL METHACRYLATE FROM ACETONE CYANOHYDRIN

1. Basic Process

The reaction of ACN to MMA involves the formation of methacrylamide sulfate from ACN. The methacrylamide sulfate is then reacted with methanol to form MMA. The reactions describing this process are as follows:



(acetone cyanohydrin) (sulfuric acid) (methacrylamide sulfate)



(methacrylamide sulfate) (methanol) (MMA) (ammonium bisulfate)

Figure III-2 is a typical process flow diagram for the manufacture of MMA from ACN.[2,3,5,6] The ACN (Stream 1) is stored until it is to be fed to the hydrolysis reactors. Sulfuric acid (Stream 2) is also fed to the reactor, forming methacrylamide sulfate. The ACN is hydrolyzed in two reactors at 130°C and the ACN—sulfuric acid reaction is highly exothermic (250,000 joules/g-mole).[4] Vapors are removed from the product stream in a vapor-liquid separator and are combined with vapors

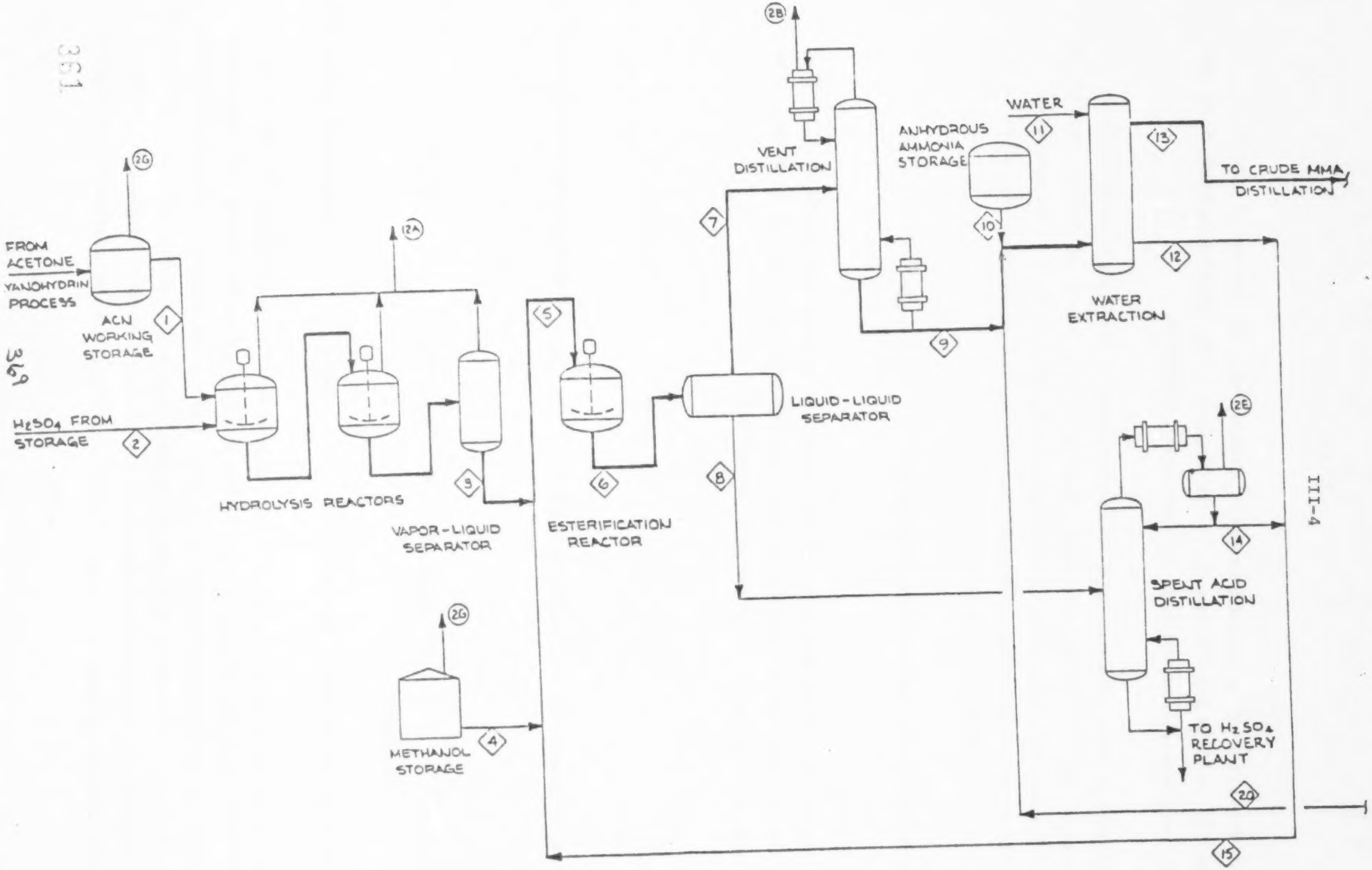

2G
FROM ACETONE YANOHYDRIN PROCESS
ACN WORKING STORAGE
1
H2SO4 FROM STORAGE
2
12A
HYDROLYSIS REACTORS
3
VAPOR-LIQUID SEPARATOR
5
ESTERIFICATION REACTOR
6
2G
METHANOL STORAGE
4
LIQUID-LIQUID SEPARATOR
7
8
2B
VENT DISTILLATION
9
ANHYDROUS AMMONIA STORAGE
10
WATER
11
WATER EXTRACTION
13
12
TO CRUDE MMA DISTILLATION
2E
14
SPENT ACID DISTILLATION
TO H2SO4 RECOVERY PLANT
20
15

Fig. III-2. Flow Diagram for the Manufacture of Methyl Methacrylate from Acetone Cyanohydrin

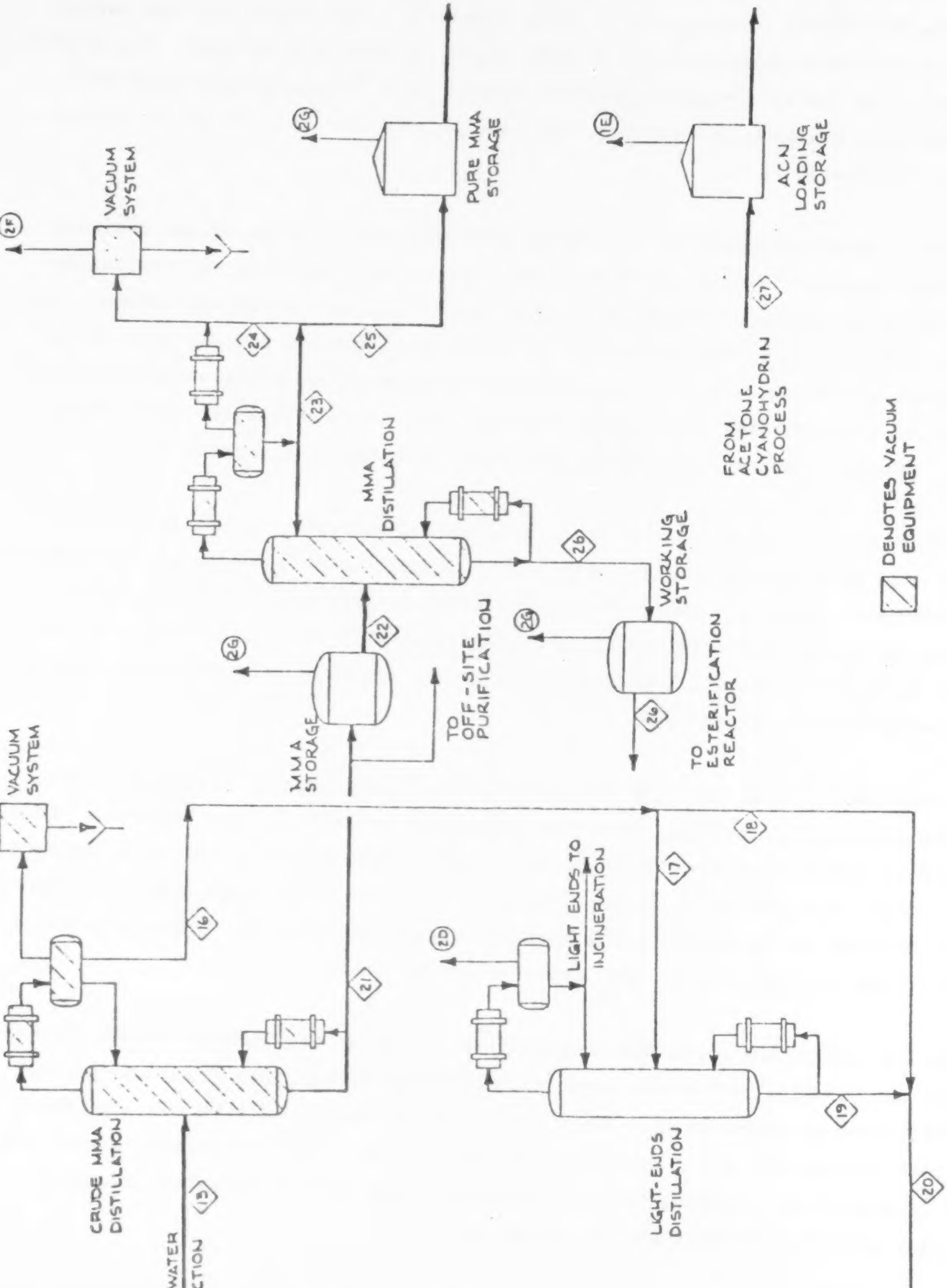

FROM WATER EXTRACTION
13
CRUDE MMA DISTILLATION
2C
VACUUM SYSTEM
16
21
17
18
19
20
LIGHT-ENDS DISTILLATION
2D
LIGHT ENDS TO INCINERATION
MMA STORAGE
TO OFF-SITE PURIFICATION
2G
22
MMA DISTILLATION
23
24
25
26
2F
VACUUM SYSTEM
2G
PURE MMA STORAGE
2G
WORKING STORAGE
TO ESTERIFICATION REACTOR
FROM ACETONE CYANOHYDRIN PROCESS
27
1E
ACN LOADING STORAGE
DENOTES VACUUM EQUIPMENT

Fig. III-2. (Continued)

from the hydrolysis reactor vent to form stream 2A. The vapors are the carbon monoxide formed by decomposition of ACN, traces of ACN, and acetone. The product (Stream 3) is fed to the esterification reactor with fresh methanol (Stream 4) and recovered methanol (Stream 14). The reactor effluent is a two-phase liquid mixture (Stream 6).

The light phase (Stream 7) is distilled in a vent distillation column designed to remove dissolved carbon monoxide; then, after the light phase is neutralized with anhydrous ammonia (Stream 10), it is fed to a water extraction column. MMA and methacrylic acid recovered later in the process (Stream 20) are also fed to the water extraction column. The raffinate (Stream 13) from the water extraction column contains the MMA and similar organics; the extract (Stream 12) contains water, ammonia bisulfate, methanol, and other water-soluble compounds.

The heavy phase (Stream 8) from the liquid-liquid separator is distilled in a spent acid distillation column, where light organics such as methanol are removed (Stream 14). These are combined with the extract (Stream 12) from the water extraction column and recycled to the esterification reactor. Bottoms from the spent acid distillation column are routed to the sulfuric acid recovery plant or to ammonia sulfate production.

The raffinate (Stream 13) from the water extraction column is distilled in a vacuum distillation column, where the light ends (Stream 16) are removed . This stream is split, with some of it being recycled (Stream 18) to the water extraction column and some of it further distilled to remove the light ends to prevent their buildup in the system. The bottoms (Stream 19) from the light-ends distillation column are recycled to the water extraction column.

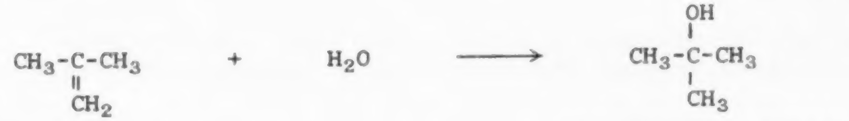
Crude MMA leaves the crude MMA distillation column as the bottoms stream (Stream 21), which can be distilled at the production location or be transported for further purification at other sites. The distillation proceeds under vacuum, and the bottoms (Stream 26) are recycled to the MMA process. The distillate is pure MMA and is stored for shipping and/or processing. ACN that is marketed (Stream 27) is also stored in preparation for shipping.

363 Inhibitors are used to prevent polymerization of the MMA under purification and storage, which vary from site to site.

D. FUTURE PROCESSES

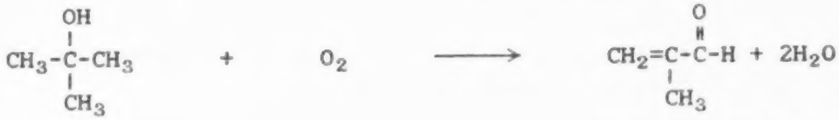
Recent literature indicates that no new MMA plants will use the ACN route as described above. Companies now entering the MMA business (such as Oxirane International and Vistron Corp.) use oxidation technology based on isobutylene, and the established companies are actively investigating this technology. The isobutylene route is expected to be less expensive compared with the ACN process.[7]

The process chemisty is described below:



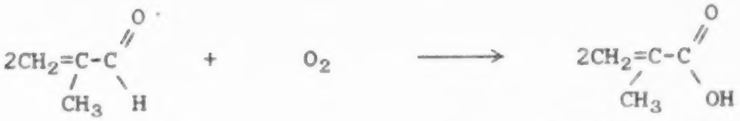
$$CH_3\text{-}\underset{\underset{CH_2}{\|}}{C}\text{-}CH_3 + H_2O \longrightarrow CH_3\text{-}\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}CH_3 \quad (1)$$

(isobutylene) (tert-butyl alcohol)



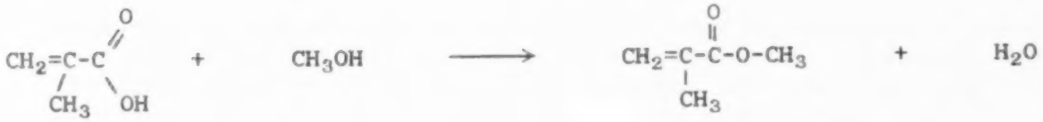
$$CH_3\text{-}\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}CH_3 + O_2 \longrightarrow CH_2{=}\underset{\underset{CH_3}{|}}{C}\text{-}\overset{\overset{O}{\|}}{C}\text{-}H + 2H_2O \quad (2)$$

(methacrolein)



$$2CH_2{=}\underset{\underset{CH_3}{/}}{C}\text{-}C\overset{O}{\underset{H}{\lessgtr}} + O_2 \longrightarrow 2CH_2{=}\underset{\underset{CH_3}{/}}{C}\text{-}C\overset{O}{\underset{OH}{\lessgtr}} \quad (3)$$

(methacrylic acid)



$$CH_2{=}\underset{\underset{CH_3}{/}}{C}\text{-}C\overset{O}{\underset{OH}{\lessgtr}} + CH_3OH \longrightarrow CH_2{=}\underset{\underset{CH_3}{|}}{C}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_3 + H_2O \quad (4)$$

(methyl methacrylate)

Reaction 1 proceeds over an acidic ion-exchange catalyst at less than 100°C. Both reactions 2 and 3 occur at about 300°C and at about 14.1 kPa. Conversions and selectivities of reactions 2 and 3 range from 80 to 90%. Reaction 4 occurs at 400°C, with conversions and selectivity at 80%. The overall yield is reported to be 58%. All steps are exothermic and reaction by-products are acetic acid (0.05 kg/kg of MMA), acetone (0.01 kg/kg of MMA), and carbon dioxide.[7]

Emission information and further process details are not available at this time.

E. REFERENCES*

1. W. J. Svirbely and J. R. Roth, "Carbonyl Reactions. I. The Kinetics of Cyanohydrin Formation in Aqueous Solution," Journal of the American Chemical Society 75, 3106—11 (1955). Cited in: R. G. Denney, Methacrylic Acid—Methacrylic Esters, Report No. 11, A private report of the Process Economics Program, Stanford Research Institute, Menlo Park, CA (May 1966).

2. Rohm & Haas, Emissions Inventory Questionnaire, submitted to Texas Air Control Board, Mar. 19, 1976.

3. J. W. Blackburn, IT Enviroscience, Inc., Trip Report on Visit to Rohm & Haas Co., Deer Park, TX, Nov. 1, 1977 (on file at the ESED, EPA, Research Triangle Park, NC).

4. D. C. Thomas, Methacrylic Acid—Methacrylic Esters, Report No. 11A, A private report of the Process Economics Program, Stanford Research Institute, Menlo Park, CA (May 1974).

5. J. W. Blackburn, IT Enviroscience, Inc., Trip Report on Visit to E. I du Pont de Nemours & Co., Memphis, TN, Jan. 10, 1978 (on file at the ESED, EPA, Research Triangle Park, NC).

6. Nonconfidential information provided to EPA on May 1978 from CY/RO Industries, Wayne, NJ (on file at the ESED, EPA, Research Triangle Park, NC).

7. J. C. Davis, "Big Changes in Store for Methyl Methacrylate," Chemical Engineering 85(15), 25—27 (1978).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS AND APPLICABLE CONTROL SYSTEMS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. GENERAL

Emission data from the three domestic producers of MMA and ACN are presented in Tables IV-1 and IV-2. The ACN and MMA process flowsheets (Figs. III-1 and III-2) are used as model processes, and the emission data from the three producers are arranged to fit the flowsheets. No model-plant or average emission rate for these processes is included in this study since data were obtained for all three domestic producers and future increases in MMA production will involve oxidation technology based on isobutylene.

The uncontrolled emissions from normal process vents are based on data obtained from the producers. The controlled emissions from the normal process vents are based on the current level of control now used in the industry and noted later in the text.

Emissions from the plants are classified as process, storage and handling, secondary, and fugitive emissions. Process and secondary emissions for the plants are based on data obtained from plant site visits and reports submitted to the EPA.[1—4] Fugitive and storage and handling emissions are not included in this report since emission rates and controls for the SOCMI are discussed in separate EPA documents.

B. ACETONE CYANOHYDRIN PROCESS (Fig. III-1, Table IV-1)

The normal process emission occurs from the following sources:

Table IV-1. Uncontrolled and Controlled VOC Emissions from Production of Acetone Cyanohydrin

Source	Stream Designation (Fig.III-1)	Uncontrolled Emission Ratio (kg/Mg)*	Control Device or Technique	Emission Reduction (%)	Controlled Emission Ratio (kg/Mg)*
CY/RO Industries, Fortier, LA (36 Gg/yr)		No data available			
Du Pont, Memphis, TN (109 Gg/yr)					
Reactor off-gas	1A	0.039	Condenser	90	0.004
Recovery columns	1B,1C,1D	1.17	None		1.17
Rohm & Haas, Deer Park, TX (300 Gg/yr)					
Reactor off-gas	1A	No data	Flare		
Acetone evaporation vaccum vent	1B	0.004	None		0.004
Recovery column	1C,1B	0.004	None		0.004

*kg of VOC per Mg of acetone cyanohydrin produced.

Table IV-2. Uncontrolled and Controlled VOC Emissions from Production of Methyl Methacrylate

Source	Stream Designation (Fig.III-2)	Uncontrolled Emission Ratio (kg/Mg)*	Control Device or Technique	Emission Reduction (%)	Current Emission Ratio (kg/Mg)*
CY/RO Industries, Fortier, LA (36 Gg/yr)					
Reactor vent	2A				0.0
Vent distillation	2B				0.954
MMA and light-ends distillation	2C,2D				11.8
Acid distillation	2E				1.09
MMA purification	2F				2.1
Total					15.9
Du Pont, Memphis, TN (109 Gg/yr)					
Reactor vent and acid distillation	2A,2E	6.62	None		6.62
Vent, MMA, and light-ends distillation	2B,2C,2D	4.74	None		4.74
MMA purification	2F	2.65	Condenser	96.7	0.087
Total					11.4
Rohm & Haas, Deer Park, TX (300 Gg/yr)					
Reactor vent and vent, MMA, and light-ends distillation	2A,2B,2C,2D	21.0	Flare	99+	
Acid distillation	2E				0.007
MMA purification	2F				19
Total					19.0

*kg of VOC per Mg of methyl methacrylate produced.

1. Acetone Cyanohydrin Reactor (Vent 1A)

Information from one methyl methacrylate producer[1] indicates that the reactor off-gas rate is low. The VOC emission is composed of acetone and hydrogen cyanide and is curently being controlled by condensers or is sent to a flare.

2. Purification and Recovery Columns (Vents 1B, 1C, and 1D)

To reduce the acetone loss from the product distillation columns and acetone recovery column, condensers are used. These condensers are not considered to be emission control devices unless they operate beyond economic optimum. CY/RO Industries passes these vent gases through an incinerator.

3. Secondary Emissions

Secondary emissions related to ACN production are from handling of sulfate salts and from wastewater from the acetone recovery distillation column. One manufacturer[1] states that there are no secondary emissions related to the manufacture of acetone cyanohydrin.

C. METHYL METHACRYLATE PROCESS (Fig. III-2, Table IV-2)

1. Hydrolysis Reactor (Vent 2A)

The emissions from the hydrolysis reactor vent are composed primarily of sulfur dioxide and carbon monoxide and other reaction by-products. No data are available for emissions from this vent, since they are combined with other vent emissions. Currently the emissions are mixed with other vent streams and are sent to a flare or are not being controlled.

2. Distillation Vents (2B, 2C, 2D, 2E, 2F)

The gases from the vent distillation, crude MMA, light-ends, spent acid, and product-MMA columns are composed of noncondensables that are dissolved in the feed to the columns, of the VOC that are not condensed, and, for columns operated under vacuum, of the air that leaks into the column and is removed by a vacuum jet system.

The emissions are primarily controlled by condensers, which are usually included as part of the processing condensers. Current emission rates are reported in Table IV-2; some of the data on the uncontrolled emissions are not available.

In one case some of the vent emissions are combined and sent to a flare, which achieves 99+% VOC reduction.[2]

3. Secondary Emissions

Secondary emissions related to MMA production are from organic wastes routed to an incinerator or acid recovery unit, from intermittent aqueous wastes that are sent to a sewer, and from spent acid and aqueous wastes that are sent to sulfuric acid recovery.[1]

The organic wastes generated are polymeric material formed during MMA production, acid recovery, or incineration. The polymeric formation rate is estimated at 0.002[2] and 0.018[1] (kg of polymer/kg of MMA product); the polymer goes to landfill or incineration.

The spent acid has been reported to contain 0.5% VOC[5] to 10% VOC,[1] including methyl methacrylate, methacrylic acid, methyl formate, methanol, and acetone. Emissions from sulfuric acid recovery can be a significant fraction of the controlled VOC emission levels. Little or no organic emission data exist for various types of acid recovery units when the feed stream contains organics. These secondary emission and control systems will be discussed in a future EPA report.

D. ESTIMATED EMISSIONS FOR THE INDUSTRY

At the current level of control the VOC emissions for the acetone cyanohydrin industry are estimated at 193 Mg/yr* for the production dedicated to methyl methacrylate (approximately 80% of the ACN produced).

At the current level of control the VOC emissions are estimated at 6020 Mg* for the 1978 methyl methacrylate production (domestic) of 370 Gg/yr.

If all methyl methacrylate were produced by the lowest emitting process in current operations, the total domestic VOC emissions, including ACN production, would be reduced from 6213 Mg/yr to 4219 Mg/yr. Most of the reduction could be accomplished by condensing the emissions from the vacuum systems. The cost or practicality of incorporating additional controls to existing processes has not been evaluated in this abbreviated product report.

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*Does not include fugitive, secondary, and storage and handling emissions.

As discussed in Sect. III-D, it is anticipated that no new methyl methacrylate processes will be patterned after the processes currently in operation.

The preceding emission estimates for the industry are based on the following assumed criteria: Du Pont's Belle, WV, plant has the same level of emission as its Memphis, TN, plant; all the production facilities are operating at the same percent of capacity.

E. REFERENCES*

1. J. W. Blackburn, IT Enviroscience, Inc., Trip Report on Visit to E. I. du Pont de Nemours & Co., Memphis, TN, Jan. 10, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. J. W. Blackburn, IT Enviroscience, Inc., Trip Report on Visit to Rohm & Haas Co., Deer Park, TX, Nov. 1, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. CY/RO Industries, letter dated May 4, 1978, in response to EPA's request for information on emission data on methyl methacrylate production facilities.

4. Rohm & Haas Company, emissions data in Emissions Inventory Questionnaire, submitted to Texas Air Control Board, Mar. 19, 1976.

5. L. D. Johnson, Rohm & Haas Co., letter dated June 21, 1979, to D. R. Patrick, EPA.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX A

Table A-1. Physical Properties of Acetone Cyanohydrin[a]

Molecular formula	C_4H_7NO
Molecular weight	85.11
Physical state	Liquid
Vapor pressure	10 mm Hg at 70°C[b] or 0.3 mm Hg at 20°C[c]
Vapor specific gravity	2.93
Boiling point	82°C at 23 mm Hg
Melting point	-20°C
Density	0.932 at 20°C/4°C
Water solubility	Very soluble; decomposes in H_2O

[a] From: J. Dorigan, B. Fuller, and R. Duffey, "Acetone Cyanohydrin," p AI-22 Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C), MTR-7248, Rev. 1, Appendix I, MITRE Corp., McLean, VA (1976).

[b] According to data developed by Rohm and Haas Co.

[c] According to a Chemical Manufacturing Association member company.

Table A-2. Physical Properties of Methyl Methacrylate*

Molecular formula	$C_5H_8O_2$
Molecular weight	100.13
Physical state	Liquid
Vapor pressure	40 mm Hg at 25.5°C
Vapor specific gravity	3.45
Boiling point	100 to 101°C at 760 mm Hg
Melting point	-48°C
Density	0.9440 at 20°C/4°C
Water solubility	Slight

*From: J. Dorigan, B. Fuller, and R. Duffey, "Methyl Methacrylate," p AIII-204 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F-N), MTR-7248, Rev. 1, Appendix III, MITRE Corp., Mclean, VA (1976).

REPORT 6

CHLOROPRENE

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ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

September 1980

This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	$1\ Tg = 1 \times 10^{12}$ grams
G	giga	10^{9}	$1\ Gg = 1 \times 10^{9}$ grams
M	mega	10^{6}	$1\ Mg = 1 \times 10^{6}$ grams
k	kilo	10^{3}	$1\ km = 1 \times 10^{3}$ meters
m	milli	10^{-3}	$1\ mV = 1 \times 10^{-3}$ volt
μ	micro	10^{-6}	$1\ \mu g = 1 \times 10^{-6}$ gram

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II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Chloroprene production was selected for study because the total estimated emissions of volatile organic compounds (VOC) from the chloroprene industry were initially projected to be significant. However, upon further study it was determined that the major portion of the projected emissions occur in further processing of the chloroprene in the manufacture of neoprene rubber.

Chloroprene is a flammable liquid boiling at 59.4°C, and its vapors are a health hazard. Appendix A gives the pertinent physical properties of chloroprene and butadiene, its organic raw material.

B. USAGE AND GROWTH

Essentially the entire production of chloroprene is consumed in the manufacture of neoprene rubber. Uses for neoprene are mainly in oil-resistant rubber goods, automobile components, and wire and cable coatings (see Table II-1).[1]

The 1979 domestic neoprene capacity is reported to be 240 Gg/yr (see Table II-2).[2—5]

In 1978 the production of neoprene rubber was estimated to be 160 Gg. Typically, 25—35% of the production is for export. Allowing for a 10% yield loss in the conversion of chloroprene to neoprene, a capacity utilization of chloroprene for 1978 is estimated to have been 68%. Based on a projected growth rate of 2.5 to 3.5% for the period 1978—1982 the demand for neoprene will reach 177 to 184 Gg in 1982 and the capacity utilization of chloroprene will be 75 to 78%.[2]

C. DOMESTIC PRODUCERS

There are two domestic producers of chloroprene at three locations (see Table II-2).[2—5]

1. Denka Chemical Corporation

This facility, located in Houston, TX, was formerly owned and operated by Petro-Tex Chemical Corporation and was sold to Denka Chemical Corporation in July 1977.[5] The process is based on chlorination of butadiene.[3]

2. E. I. du Pont de Nemours and Company

The plants at La Place, LA, and Victoria, TX, are both based on chlorination of butadiene. The facilities at Victoria, TX, make both adiponitrile and chloroprene via chlorination of butadiene, which allows some flexibility in operation.[2]

D. REFERENCES*

1. "Polychloroprene (Neoprene) Elastomers," pp. 525.5020A—D in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1977).

2. T. F. Killilea, "Butadiene," pp. 300.5802J—L in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (October 1979).

3. A. J. Meyer, Denka Chemical Corp., letter dated Mar. 26, 1979, in response to EPA request for information on emissions from chloroprene production facilities.

4. H. A. Smith, E. I. du Pont de Nemours and Co., letter dated Nov. 28, 1978, in response to EPA request for information on emissions from chloroprene production facilities.

5. R. D. Pruessner, Petro-Tex Chemical Corp., letter dated Sept. 29, 1978, in response to EPA request for information on emissions from chloroprene production facilities.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

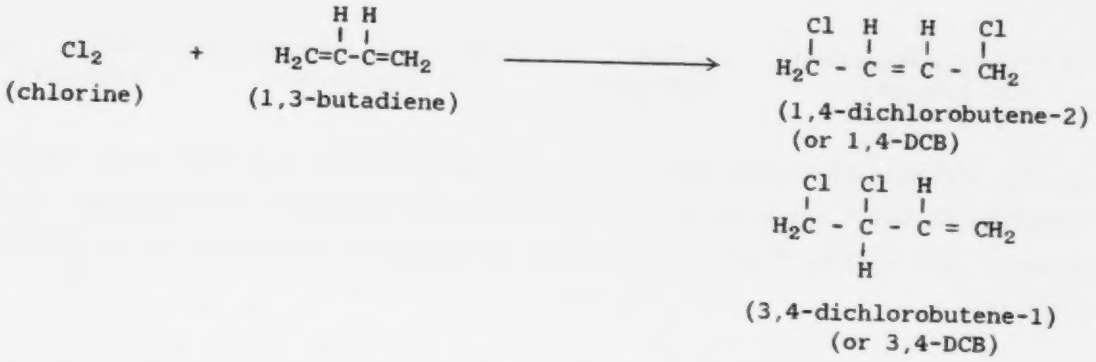
A. INTRODUCTION

Chloroprene has been produced commercially in the United States since 1932. All chloroprene production was based on acetylene until 1970, at which time butadiene-based production was started. Since 1972 all production has been via the butadiene-based process.[1] This report is concerned with only the butadiene-based process.

B. CHEMISTRY

The commercial route from 1,3-butadiene (butadiene) to 2-chloro-1,3-butadiene (chloroprene) requires three chemical process steps: chlorination to form mixed isomers of dichlorobutene, isomerization of the undesired isomer to yield only the desired isomer, and dehydrochlorination of the desired isomer to chloroprene.[2]

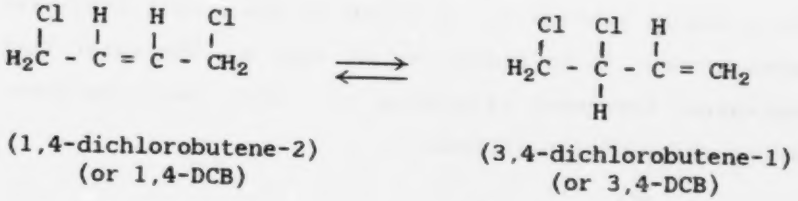
1. Chlorination



$$Cl_2 + H_2C{=}\overset{H}{C}{-}\overset{H}{C}{=}CH_2 \longrightarrow H_2\overset{Cl}{C}-\overset{H}{C}=\overset{H}{C}-\overset{Cl}{C}H_2 \quad + \quad H_2\overset{Cl}{C}-\underset{H}{\overset{Cl}{C}}-\overset{H}{C}=CH_2$$

In addition to the above several other products are formed in the reactor: tetrachlorobutane, which is formed by further chlorination of the DCBs; HCl and chlorobutadienes, which are formed by decomposition of the DCBs; chlorobutenes and chlorobutanes, which are formed from impurities in the butadiene; and CO_2 and H_2O, which are formed from any oxygen present.[2]

2. Isomerization

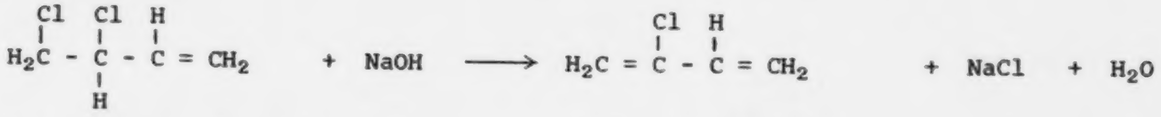


$$H_2\overset{Cl}{C}-\overset{H}{C}=\overset{H}{C}-\overset{Cl}{C}H_2 \rightleftarrows H_2\overset{Cl}{C}-\underset{H}{\overset{Cl}{C}}-\overset{H}{C}=CH_2$$

In the presence of a catalyst 1,4-DCB is converted to 3,4-DCB, producing a mixture that under equilibrium conditions consists of essentially equal parts of each isomer. By the combined processes of distillation and isomerization the undesired isomer formed in chlorination is consumed and only the desired isomer is yielded.

During the process of isomerization small quantities of the dichlorobutenes are decomposed to yield HCl and chlorobutadiene. Some of the chlorobutadiene is polymerized to nonvolatile products that are ultimately wasted, and the remainder is vented from the process along with the HCl that is formed and the low-boiling chlorinated organic compounds that were formed in the chlorinator.[2,3]

3. Dehydrochlorination



$$\mathrm{H_2\overset{Cl}{C}} - \underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}} - \overset{\mathrm{H}}{\mathrm{C}} = \mathrm{CH_2} + \mathrm{NaOH} \longrightarrow \mathrm{H_2C} = \overset{\mathrm{Cl}}{\mathrm{C}} - \overset{\mathrm{H}}{\mathrm{C}} = \mathrm{CH_2} + \mathrm{NaCl} + \mathrm{H_2O}$$

(3,4-dichlorobutene-1) (or 3,4-DCB) (sodium hydroxide) (2-chloro-1,3-butadiene) (or chloroprene) (sodium chloride) (water)

In the presence of sodium hydroxide solution (caustic) and under mild conditions of temperature the 3,4-DCB is dehydrochlorinated to 2-chloro-1,3-butadiene (chloroprene). The sodium chloride brine that is formed is discarded, as is any excess caustic.

C. PROCESS DESCRIPTION

The process flow diagram shown in Fig. III-1 represents a typical continuous process for the manufacture of chloroprene based on chlorination of butadiene. This process was assembled from limited available sources.[2—6] It does not necessarily represent an actual chloroprene plant but typifies the processing steps of a complete plant and its emission sources.

1. Butadiene (BD) Drying

Butadiene, received as a liquid (stream 1), is dried by azeotropic distillation, allowing any inert gases present to be discharged at vent A. The water that is removed is sent to wastewater treatment (discharge G). Dry, inert-gas-free, butadiene is forwarded to chlorination (stream 2).

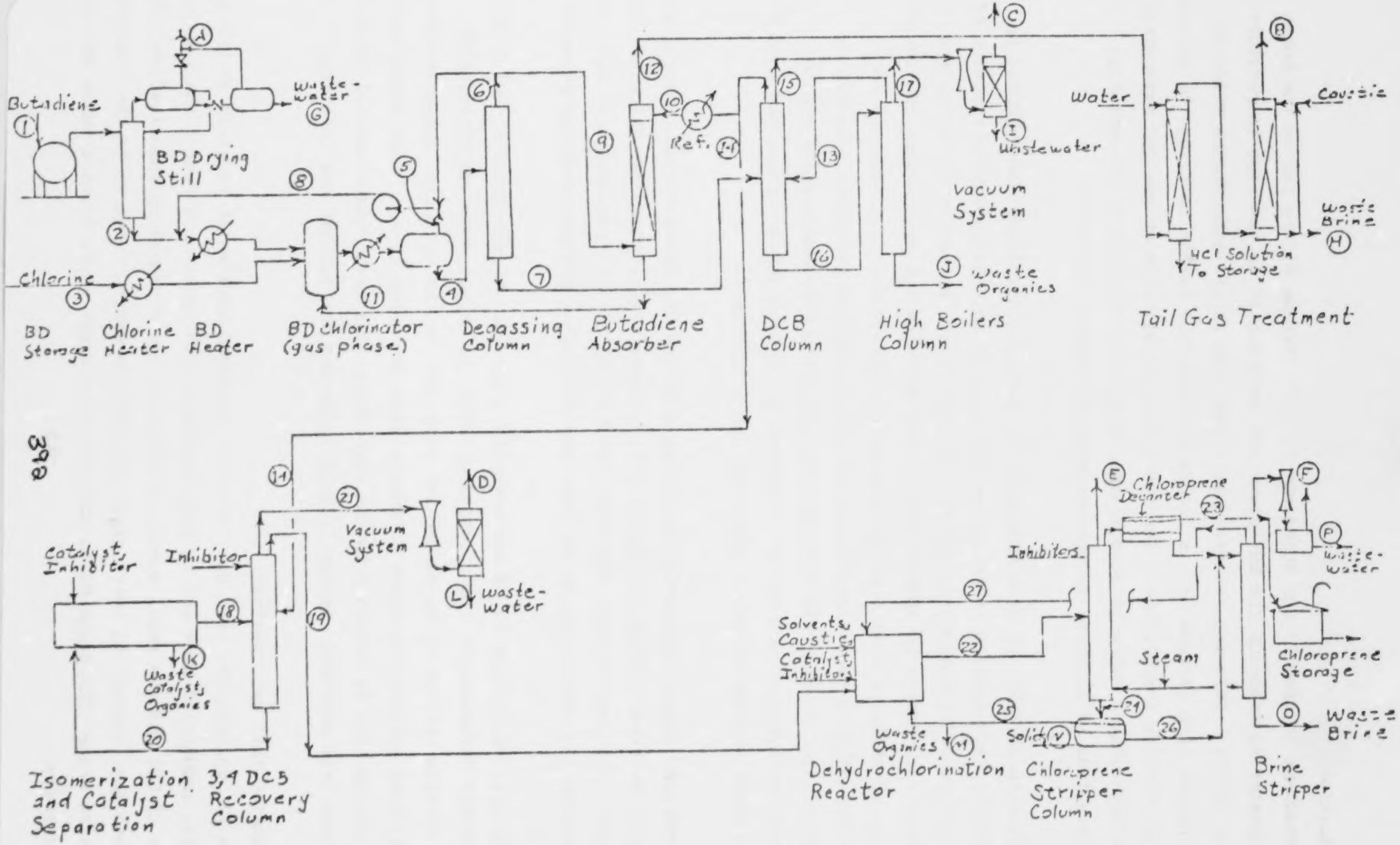

Butadiene
①
BD Storage
A
waste-water
G
BD Drying Still
②
Chlorine
③
Chlorine Heater
BD Heater
⑧
⑤
BD chlorinator (gas phase)
⑪
④
⑥
Degassing Column
⑦
⑨
Butadiene Absorber
⑫
⑩
Ref.
14
DCB Column
⑮
⑬
⑯
⑰
High Boilers Column
C
I
Wastewater
Vacuum System
J
waste Organics
Water
R
Caustic
Waste Brine
H
HCl Solution To Storage
Tail Gas Treatment
14
Catalyst, Inhibitor
Inhibitor
⑱
K
Waste Catalyst, Organics
⑳
Isomerization and Catalyst Separation
3,4 DCB Recovery Column
㉑
⑲
Vacuum System
D
L
waste-water
Solvents, Caustics, Catalyst, Inhibitors
㉗
㉒
㉕
Waste Organics
M
Dehydrochlorination Reactor
Inhibitors
E
Chloroprene Decanter
㉓
Steam
㉔
V
Solid
㉖
Chloroprene Stripper Column
F
P
waste-water
Chloroprene Storage
O
Waste Brine
Brine Stripper

Fig. III-1. Flow Diagram for Chloroprene from Butadiene

Reproduced from best available copy.

2. Chlorination

Dry butadiene (stream 2) and butadiene recycle (stream 8) are fed to the butadiene heater to vaporize the butadiene and to bring it to reaction temperature (250 to 300°C). Chlorine, received as a gas from an off-site liquid chlorine vaporization step (stream 3), is fed to the chlorine heater to bring the chlorine also to reaction temperature. The two preheated gas streams are fed separately to the chlorinator, wherein good mixing is quickly imparted to prevent high concentrations of chlorine in the presence of organic materials.

The reaction of chlorine with butadiene to form the dichlorobutenes (DCBs) is exothermic. At elevated temperatures the rate of the decomposition reaction of DCBs to form chlorobutadienes and HCl is excessive. Butadiene is fed to the chlorinator in excess to absorb some of the exotherm and to minimize the further reaction of chlorine with DCBs to form tetrachlorobutane. In addition to excess butadiene a controlled stream of process liquid (stream 11) is fed to the chlorinator to moderate the reaction temperature by evaporative cooling. The reaction products are partly condensed by cooling and are separated into a liquid phase (stream 4) and a vapor-gas phase (stream 5).

The condensed liquid (stream 4) is stripped in the degassing column, thereby producing an overhead stream (6) that contains inert gases, unreacted chlorine, HCl, butadiene, chlorobutadienes and other low-boiling chlorinated organics, and a bottoms stream (7) that contains the DCBs and the higher boiling reaction products.

A major portion (stream 8) of the combined vapor-gas streams 5 and 6, which result from excess butadiene in the chlorinator feed, is recycled to the chlorinator. A small portion (stream 9) is purged and then sent to the butadiene absorber, where chilled DCBs (stream 10) scrub butadiene from the purge stream. The butadiene-laden (DCB) stream (11) is returned to the chlorinator for temperature control while the butadiene-lean overhead stream (12) is forwarded for further gas treatment.

3. Chlorinator Tail Gas Treatment

Stream 12, chlorinator tail gas, is first scrubbed with water to yield an HCl solution for industrial uses and is then scrubbed with caustic to remove the remaining traces of HCl and the small amount of chlorine not consumed in chlorination. The scrubbed gas, containing inert gases and VOC, is vented (vent B) to the atmosphere. The waste brine (discharge H) is combined with other waste brine streams for suitable disposal.

4. Dichlorobutene (DCB) Distillation

The bottoms stream (7) from the degassing column, along with the overhead stream (13) from the high-boilers column, is fractionated in the DCB column to produce an overhead product of mixed DCBs. A small portion of the overhead product from the DCB column (stream 10) is chilled and sent to the butadiene absorber, while the remainder (stream 14) is forwarded to isomerization. Inert gases, HCl, and some chlorobutadienes (stream 15) are sent to the vacuum system. A water scrubber is used on the tail gas from the vacuum system to absorb the HCl before the remaining gases are released (vent C) to the atmosphere. Wastewater (discharge I) resulting from water scrubbing is sent to wastewater treatment.

The bottoms stream (16) from the DCB column is forwarded to the high-boilers column, where the remaining DCBs are recovered overhead and returned (stream 13) to the DCB column. Inert gases used in the control of vacuum operation and HCl and chlorobutadienes from decomposition of the DCBs are forwarded to the vacuum system through stream 17. The gases leaving the vacuum system are scrubbed with water to remove traces of HCl before being released (vent C) to the atmosphere. Wastewater (discharge I) from water scrubbing is sent to wastewater treatment. Nonvolatile waste products formed during chlorination and distillation are removed from the system at discharge J.

5. Isomerization and 3,4-DCB Recovery

Streams 14 and 18 are fractionated in the 3,4-DCB recovery column to recover 3,4-DCB as an overhead product (stream 19) and 1,4-DCB as a bottoms product (stream 20). The 3,4-DCB recovery column is operated under vacuum to maintain a lower temperature in order to retard the isomerization of 3,4-DCB back to 1,4-DCB. Polymerization inhibitors are added to retard the formation of polymers from any chlorobutadienes resulting from breakdown of the DCBs. The vent gas (stream 21) from the distillation process contains HCl, chlorobutadiene, and the inert gases resulting from vacuum operation. After passing through the vacuum system the vent gases are scrubbed with water to absorb the HCl before they are released (vent D) to the atmosphere. Wastewater (discharge L) is sent to wastewater treatment.

Stream 20 is mixed with catalysts in the isomerization and catalyst removal step to enable some of the 1,4-DCB isomer to undergo rearrangement and to form 3,4-DCB. In the process some of the DCBs decompose, forming HCl and chlorobutadienes. Polymerization inhibitors are added to retard the formation of chlorobutadiene polymers. After isomerization the mixture of DCBs is separated from the catalyst and wastes and is forwarded (stream 18) to the 3,4-DCB recovery column. Spent catalyst, inhibitors, and nonvolatile organic wastes, including polymers, are purged at discharge K.

6. Dehydrochlorination (DHC) and Chloroprene Recovery

The purpose of the dehydrochlorination (DHC) reactor process is to remove HCl from the 3,4-DCB molecule and form 2-chloro-1,3-butadiene (chloroprene). Inhibitors are used to retard the isomerization of 3,4-DCB back to 1,4-DCB, which would subsequently dehydrochlorinate to the wrong chlorobutadiene, and to retard the formation of polymers from both chlorobutadienes.

3,4-Dichlorobutene (stream 19) is fed to the DHC reactor along with caustic, catalysts, reaction-promoting solvents, and inhibitors. The flow (stream 22) from the DHC reactor is fed to the chloroprene stripper, where chloroprene is recovered as the chloroprene-water azeotrope by steam distillation. After condensation and decantation the chloroprene product (stream 23) is sent to storage and the water layer is sent to the brine stripper. Polymerization inhibitors are also fed to the distillation column to inhibit the formation of polymers. Inert gases present in the feed streams are released to the atmosphere at vent E.

The bottoms (stream 24) from the chloroprene stripper contain large amounts of sodium chloride brine, high-boiling solvents, unreacted DCB, and residual chloroprene and are sent to the decanter for separation of oils, brine, and polymer wastes. After decantation most of the oil phase (stream 25) is returned to the DHC reactor, while a portion (discharge M) is purged as a waste liquid. The small amount of polymer waste that is formed is periodically removed (discharge N). Both of these waste materials are disposed of by incineration. The organic-laden brine layer (stream 26) and the water from the chloroprene decanter are then fed to the brine stripper, where the solvent, unreacted DCB, and chloroprene are recovered (stream 27) by steam distillation and returned to the DHC reactor. This step requires vacuum distillation, and in-leakage air, along with entrained gases, is released to the atmosphere at vent F. Disposal of the waste brine (discharge O) is by deep well or other appropriate means.

D. PROCESS VARIATIONS

Since the process described above typifies the processing steps required for a complete chloroprene plant but does not necessarily represent an actual facility, variations from the typical process are therefore to be expected.

Significant variation from the typical process can occur as different catalysts and inhibitors are used; as an example, if a less active inhibitor or higher temperatures are used in DCB distillation, considerably more DCB will decompose into HCl and chlorobutadiene. This may then require different operating conditions and different equipment configuration to obtain an economic yield and require different methods of emission control.

E. REFERENCES*

1. T. F. Killilea, "Butadiene," pp. 300.5802J—L in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (October 1979).

2. P. L. Morse, Chloroprene, pp. 17—71, in Report No. 67, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (December 1970).

3. A. J. Meyer, Denka Chemical Corp., letter dated Mar. 26, 1979, in response to EPA request for information on emissions from chloroprene production facilities.

4. H. A. Smith, E. I. du Pont de Nemours and Co., letter dated Nov. 28, 1978, in response to EPA request for information on emissions from chloroprene production facilities.

5. W. J. Touhey, E. I. du Pont de Nemours and Co., letter dated Sept. 14, 1979, in response to EPA request for information on emissions from chloroprene production facilities.

6. Telephone conversation of S. W. Dylewski, IT Enviroscience, Inc., with W. J. Touhey, E. I. du Pont de Nemours and Co., Nov. 8, 1979.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. TYPICAL PLANT

The typical plant developed for this study has a capacity of 86 Gg/yr based on 8760 hr of operation* per year, which is the capacity of one of the currently operating plants.[1,2]

The quality of raw materials used in this study is typical of commercial materials in current use. The composition of butadiene was taken as 99.5% 1,3-butadiene and 0.5% butenes,[3] with 700 ppm of dissolved inert gas. Chlorine composition was taken as 99.8+% Cl_2, with 60 ppm of nonvolatiles[4] and 800 ppm of dissolved nitrogen.

B. SOURCES AND EMISSIONS

Uncontrolled emission of volatile organic chemicals (VOC) from process sources in chloroprene production are summarized in Table IV-1 and are discussed below. The locations of the emission sources are shown in Fig. III-1.

1. Butadiene Dryer Vent

The inert gas present in the butadiene feed is released during azeotropic drying of butadiene. The inert gas and some butadiene carried with it are released at vent A. The quantity of emission is related to production, as well as to the nitrogen content of butadiene raw material.

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*Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and the annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations the error introduced by assuming continuous operation is negligible.

Table IV-1. VOC Emissions from Uncontrolled Sources in Typical Chloroprene Plant

Emission Source	Stream Designation (Fig.III-1)	VOC Emissions	
		Ratio (g/kg)[a]	Rate (kg/hr)[b]
Butadiene dryer vent	A	1.216	11.96
Chlorination vent	B	0.237	2.33
DCB distillation vent	C	3.92	38.56
Isomerization and 3,4-DCB recovery vent	D	0.144	1.42
Chloroprene stripper vent	E	0.156	1.53
Brine stripper vent	F	0.156	1.53
		5.829	57.33

[a] g of emission per kg of chloroprene produced.

[b] Based on 8760-hr/yr operation.

2. Chlorination Vent

Nitrogen present in the chlorine feed and HCl formed during the reaction must be purged from the reactor system. The purged gases carry with them butadiene, other VOC, and some unreacted chlorine. The purged gas stream is scrubbed with water and then with caustic, which removes the acid gases; however, the butadiene and most of the VOC are not condensed and are ultimately emitted at vent B. The inert content of the chlorine, the rate of decomposition of DCB to produce HCl, and the throughput rate will affect the quantity of the emissions.

3. Dichlorobutane (DCB) Distillation Vent

The gases present in the feed, inert gases used for vacuum control, air in-leakage due to vacuum operation, and HCl resulting from decomposition of DCB, must be purged from the DCB distillation system. Along with these gases low-boiling VOC, chlorobutadiene, and DCBs are also purged. The HCl is removed by water scrubbing but most of the VOC remain with the gas to be released at vent C. The rate of decomposition of DCB will affect the VOC emission to a large extent, as will the throughput rate.

4. Isomerization and 3,4-DCB Recovery Vent

The gases present in the feed, inert gases used for vacuum control, in-leakage air due to vacuum operation, and HCl resulting from decomposition of DCB must be purged from the DCB distillation system. Along with these purged gases low-boiling VOC, chlorobutadiene, and DCBs are also released. The HCl is removed by water scrubbing but most of the VOC remain with the gas to be released at vent D. The rate of decomposition of DCB will affect the VOC emission to a large extent, as will the throughput rate.

5. Chloroprene Stripper Vent

Inert gases present in the feed and in the steam used for steam distillation in the chloroprene stripper column must be vented. These gases, as well as the VOC that they carry, are released to the atmosphere at vent E.

6. Brine Stripper Vent

Inert gases present in the feed, gases in the steam used for steam distillation, air in-leakage due to vacuum operation, and gases used for vacuum control in the brine stripper must be vented. These gases and the VOC that they carry are released to the atmosphere at vent F.

7. Storage, Fugitive, and Secondary Emissions

Storage and handling, fugitive, and secondary emissions for the entire synthetic organic chemicals manufacturing industry are covered by separate EPA documents.[5—7]

C. REFERENCES*

1. H. A. Smith, E. I du Pont de Nemours and Co., letter dated Nov. 28, 1978, in response to EPA request for information on emissions from chloroprene production facilities.

2. W. J. Touhey, E. I. du Pont de Nemours and Co., letter dated Sept. 14, 1979, in response to EPA reqest for information on emissions from chloroprene production facilities.

3. A. J. Meyer, Denka Chemical Corp., letter dated Mar. 26, 1979, in response to EPA request for information on emissions from chloroprene production facilities.

4. Telephone conversation of S. W. Dylewski, IT Enviroscience, Inc., with R. E. Wing, Dow Chemical Co., Nov. 6, 1979.

5. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

6. D. G. Erikson, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

7. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. BUTADIENE DRYER VENT

One manufacturer controls the butadiene dryer vent (vent A, Fig. III-1) emissions with a flare,[1] whereby a VOC emission reduction of 99% or greater can be attained.[2] A refrigerated vent condenser may be used as a control device to accomplish a VOC emission reduction of 82% (see vent A, Table V-1). The recovered butadiene can be recycled and thereby reduce the quantity of butadiene raw material required. The installation cost of a flare system very likely is higher than that of a refrigerated vent condenser and does not provide resource recovery. However, the higher cost factor may not be a consideration if the flare is needed for other purposes.

B. CHLORINATION VENT

The VOC emission from the caustic scrubber vent (B) is mainly butadiene, which can be reduced by 90% by the vent stream being recycled back to the process. This can be done by releasing 10% of the stream to the atmosphere to purge it of undesirable organic materials and compressing and condensing the remainder, decanting the condensate, returning the organic portion to the butadiene dryer for purge of the inert gases, and sending the aqueous portion to wastewater treatment. The emissions from vent B can also be sent to a flare, where a reduction of 99% or greater can be attained.[2]

C. DICHLOROBUTENE (DCB) DISTILLATION VENT

The VOC emissions from DCB distillation vent (C) is a mixture of low-boiling VOC, chlorobutadiene, and DCB. These emissions can be controlled by refrigerated vent condensers at each of the distillation steps. The combined emission reduction is estimated to be 95%. The emissions from vent C can also be sent to a flare, where a reduction of 99% or greater can be attained.[2]

D. ISOMERIZATION AND DISTILLATION VENT

The emissions from the isomerization and distillation vent (D) are a mixture of low-boiling VOC, chlorobutadienes, and DCBs. These emissions can be controlled by a refrigerated vent condenser and will effect a 75% reduction of VOC. The emissions from vent D can also be sent to a flare, where an emission reduction of 99% or greater can be obtained.

Table V-1. VOC Emissions from Controlled Sources in Typical Chloroprene Plant

Emission Sources	Stream Designation (Fig.III-1)	Control Device or Technique	Emission Reduction (%)	VOC Emissions	
				Ratio (g/kg)[a]	Rate (kg/hr)[b]
Butadiene dryer vent	A	Refrig. condenser	82	0.220	2.16
Chlorination vent	B	Recycle with 10% purge	90	0.024	0.23
DCB distillation vent	C	Refrig. condenser	95	0.182	1.79
Isomerization and 3,4-DCB recovery vent	D	Refrig. condenser	75	0.036	0.35
Chloroprene stripper vent	E	Refrig. condenser	81	0.030	0.30
Brine stripper vent	F	Refrig. condenser	81	0.030	0.30
				0.522	5.13

[a] g of emission per kg of chloroprene produced.

[b] Based on 8760-hr/yr operation.

E. CHLOROPRENE STRIPPER VENT

The VOC emission from the chloroprene stripper vent (Vent E) is mainly chloroprene, which can be reduced by 81% by a refrigerated vent condenser.

F. BRINE STRIPPER VENT

The VOC emission from the brine stripper vent (F) is mainly chloroprene and can be reduced by 81% by a refrigerated vent condenser.

G. STORAGE AND HANDLING, FUGITIVE, AND SECONDARY EMISSIONS

Methods for the control of emissions from storage and handling, fugitive, and secondary sources for the entire synthetic organic chemicals manufacturing industry are covered by separate EPA documents.[3—5]

H. REFERENCES*

1. W. J. Touhey, E. I. du Pont de Nemours and Co., letter dated Sept. 14, 1979, in response to EPA request for information on emissions from chloroprene production facilities.

2. V. Kalcevic, IT Enviroscience, Inc., Control Device Evaluation. Flares and the Use of Emissions as Fuels (in preparation for EPA, ESED, Research Triangle Park, NC).

3. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

4. D. G. Erikson, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

5. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

The environmental impact from application of the described control systems in the typical plant would be a VOC emission reduction of 457.3 Mg/yr, as is shown in Table VI-1.*

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*Storage and handling, fugitive, and secondary emissions are not included.

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Table VI-1. Environmental Impact of Controlled Sources in a Typical Chloroprene Plant*

Emission Source	Stream Designation (Fig.III-1)	Control Device or Technique	VOC Emission Reduction (%)	VOC Emission Reduction (Mg/yr)
Butadiene dryer vent	A	Refrig. condenser	82	85.8
Chlorination vent	B	Recycle with 10% purge	90	18.4
DCB distillation vent	C	Refrig. condenser	95	322.1
Isomerization and 3,4-DCB recovery vent	D	Refrig. condenser	75	9.4
Chloroprene stripper vent	E	Refrig. condenser	81	10.8
Brine stripper vent	F	Refrig. condenser	81	10.8
				457.3

*Storage and handling, fugitive, and secondary emissions are not included.

APPENDIX A

Table A-1. Physical Properties of 1,3-Butadiene

Synonyms	Erythrene, biethylene, bivinyl, butadiene, α-β-butadiene, divinyl, pyrrolylene, vinylethylene
Molecular formula	C_4H_6
Molecular weight	54.09
Physical state	Gas
Vapor pressure	225.3 kPa at 25°C
Vapor specific gravity	1.87
Boiling point	-4.5°C
Melting point	-109.91°C
Density	0.621 at 20°C/4°C
Water solubility	Insoluble

*From: J. Dorigan et al., "1,3-Butadiene," p. A1-150 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C), MTR-7248, Appendix II, Rev. 1, MITRE Corp., McLean, VA (September 1976).

Table A-2. Physical Properties of 2-Chloro-1,3-Butadiene

Synonyms	2-Chlorobutadiene-1,3,β-chloroprene, chloroprene
Molecular formula	C_4H_5Cl
Molecular weight	88.54
Physical state	Liquid
Vapor pressure	28.7 kPa at 25°C
Vapor specific gravity	3.05
Boiling point	59.4°C
Melting point	
Density	0.9583 at 20°C/4°C
Water solubility	Slight (<10 g/liter of H_2O)

*From: J. Dorigan et al., "Chloroprene," p. AI-282 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C), MTR-7248, Appendix II, Rev. 1, MITRE Corp., McLean, VA (September 1976).

APPENDIX B

EXISTING PLANT CONSIDERATIONS

A. DATA SOURCES

Tables B-1 and B-2 represent the data on sources of emissions obtained from industry;[1—3] however, there is uncertainty about some of the data received.[1—5] (See Table B-1 footnote f and Table B-2 footnote d.) Assuming that the emission ratios from Du Pont's chloroprene plant at Victoria, TX, are the same as those from the La Place, LA, plant the total emissions from industry was 86 Mg/yr in 1978.

B. RETROFITTING CONTROLS

The industry appears to be adequately controlled, as is indicated by Tables B-1 and B-2. Additional reduction in VOC emissions may be achieved by reducing possibly excessive in-leakage air in vacuum operations. One plant[2—4] appears to have less emissions because of possible use of a catalyst that allows less severe conditions and less HCl generation. If the other plant could be converted to take advantage of this, it would further reduce emissions.

Table B-1. Control Devices and VOC Emissions from Denka (Houston, TX) Chloroprene Plant[a]

Emission Sources	Control Device or Technique	Emission Reduction (%)	Emissions Ratio (g/kg)[b]	Emissions Rate (Mg/yr)[c]
Butadiene dryer	None		0.248	8.3
Caustic scrubber (chlorinator vent)[d]	Caustic scrubber	ND[e]	0.237[f]	8.0[f]
High boilers vent (DCB distillation vent)	Refrig. condensers (2) plus water scrubber	96.5	0.128	4.3
Isomerization section vent	Refrig. condensers (2) plus oil scrubber	99.5	0.584	19.6
Chloroprene recovery and brine stripper vent	Oil absorber	100[g]		
			1.20	40.2

[a] See ref 1.

[b] g of emission per kg of chloroprene produced.

[c] Based on 8760-hr/yr operation at capacity.

[d] Items in parentheses indicate equivalent vents in typical plant.

[e] ND = no data.

[f] Emission stated to be 100% butadiene.

[g] Recovery of 100% is questionable; uncontrolled emission is 72.1 g/kg.

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Table B-2. Control Devices and VOC Emissions from Du Pont (Laplace, LA) Chloroprene Plant[a]

Emission Sources	Control Device or Technique	Emission Reduction (%)	Emissions	
			Ratio (g/kg)[b]	Rate (Mg/yr)[c]
Butadiene dryer	Flare	100		
Synthesis[d] (chlorination vent)[e]			d	d
Crude storage vent	Refrig. condenser	94	0.006	0.6
Jet vent scrubber (DCB distillation vent)	Refrig. condenser	93	0.299	28.6
Refined storage vent	Refrig. condenser	94	0.0008	0.1
Isomerization vent (isomerization and distillation vent)	Refrig. condenser	94	0.0083	0.8
Chloroprene stripper vent	Refrig. condenser	ND[f]	0.0034	0.4
Brine stripper	Refrig. condenser	ND	0.0108	1.0
			0.328	31.5

[a] See refs 2 and 3.

[b] g of emission per kg of chloroprene produced.

[c] Based on 8760-hr/yr operation at capacity.

[d] No vent reported.

[e] Items in parentheses indicate equivalent vent in typical plant.

[f] ND = no data.

C. REFERENCES*

1. A. J. Meyer, Denka Chemical Corp., letter dated Mar. 26, 1979, in response to EPA request for information on emissions from chloroprene production facilities.

2. W. J. Touhey, E. I. du Pont de Nemours and Co., letter dated Sept. 14, 1979, in response to EPA request for information on emissions from chloroprene production facilities.

3. H. A. Smith, E. I. du Pont de Nemours and Co., letter dated Nov. 28, 1978, in response to EPA request for information on emissions from chloroprene production facilities.

4. Telephone conversation of S. W. Dylewsi, IT Enviroscience, Inc., with W. J. Touhey, E. I. du Pont de Nemours and Co., Nov. 8, 1979.

5. Telephone conversation of S. W. Dylewski, IT Enviroscience, Inc., with A. J. Meyer, Denka Chemical Corp, Dec. 6, 1979.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 7

BUTADIENE

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^1
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^2
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^4
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^1
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

The production of butadiene was selected for study because preliminary estimates indicated that emissions of volatile organic compounds (VOC) from some current processes are high.

Although two isomers of butadiene occur (1,2 and 1,3), only 1,3-butadiene is of significant commercial interest. (The term butadiene in this report refers to the 1,3 isomer unless 1,2-butadiene is specifically designated.) Butadiene is a vapor at ambient conditions (see Appendix A for pertinent physical properties).

B. USAGE AND GROWTH[1]

Table II-1 shows the major butadiene uses and expected growth rates. The predominant uses are for the manufacture of elastomers, adiponitrile/HMDA (intermediates for certain nylon manufacturing processes), styrene-butadiene copolymer latexes, and ABS (acrylonitrile-butadiene-styrene) resins. Tires and tire products account for approximately half of the butadiene consumed. In addition to synthetic rubber products, it is used for carpet fibers, carpet-back coatings, paper coatings, piping, adhesives, and molded mechanical and electrical parts.[1]

The domestic butadiene production capacity by the end of 1978 was approximately 1825 Gg/yr. Domestic production in 1978 was 1598 Gg, or about 88% of year-end capacity. By the end of 1978 domestic heavy-liquid ethylene plants accounted for 56% of available domestic production capacity and net imports supplied 13% of the total demand. By 1981 imports and by-product butadiene from domestic ethylene plants are expected to account for 85% or more of the total demand. (Before 1968 almost all domestic butadiene requirements were supplied by domestic production, with dehydrogenation of n-butane and n-butenes accounting for 85% or more of the total.)

Table II-2 gives estimates for 1983 of butadiene supply sources. Production capacity by the dehydrogenation of n-butane and n-butenes is currently estimated at about 860 Gg/yr. Much of this equipment has been or will be shut down or converted to the extraction of ethylene by-product butadiene; however, the capability of producing butadiene by dehydrogenation at 45 to 60% of current dehydrogenation capacity will apparently be maintained to meet potential demand through 1981.

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Table II-1. Butadiene Usage and Growth Rate*

End Use	1978 Production (%)	Projected Average Growth Rate (%/yr) for 1978--1983
Elastomers		
SBR	44.3	1.5--2.5
Polybutadiene	19.3	2.5--3.5
Polychloroprene	6.8	2.5--3.5
Nitrile	2.6	2.0--3.0
Adiponitrile/HMDA	10.8	4.0--5.0
Styrene-butadiene copolymer latexes	7.5	3.0--4.0
ABS (acrylonitrile-butadiene-styrene) resins	5.9	5.0--6.0
Other polymers containing butadiene monomer	1.8	9.5--10.0
Other uses	1.1	7.0--10.0
Average		2.5--3.5

*See ref. 1.

Table II-2. Estimated Supply of Butadiene for 1983*

Source	Quantity (Gg)	Percent of Total
By-product production from domestic ethylene plants	1224 to 1356	68 to 69
Net imports	317 to 408	9 to 16
Dehydrogenation of n-butane and n-butenes	336 to 381	16 to 22
Total supply	1923 to 2100	100

*See ref. 1.

C. DOMESTIC PRODUCERS

As of 1977, 15 manufacturers were producing butadiene in the United States and Puerto Rico at 19 locations. Table II-3 lists the producers, locations, capacities, and processes; Fig. II-1 shows the plant locations.

The companies producing butadiene are listed below.

1. Atlantic Richfield Company

Until 1976 all butadiene was produced by dehydrogenation of *n*-butane (Houdry process). Now it is produced from only ethylene plant by-product streams. Most of the butadiene produced is sold.

2. Copolymer Rubber and Chemical Corporation

Butadiene is produced by oxidative dehydrogenation of refinery butylenes and is all captively consumed for SBR and nitrile elastomer production.

3. Dow Chemical Company

Butadiene is extracted from ethylene plant by-product streams. More than 95% is captively consumed for ABS and styrene-butadiene latex production at six domestic locations.

4. El Paso Products Company

Butadiene is produced by dehydrogenation of *n*-butane (Houdry process) and sold. A plant to produce butadiene by extraction from ethylene by-product streams is being constructed near Corpur Christi, TX. The plant will utilize dimethyl formamide for extractive distillation.

5. Exxon Corporation

Butadiene is extracted from ethylene plant by-product streams and sold.

6. Firestone Tire and Rubber Company

Butadiene is produced from *n*-butane and *n*-butenes, using Houdry and oxidative dehydrogenation processes, and is captively consumed to produce SBR, polybutadiene, and styrene-butadiene latex.

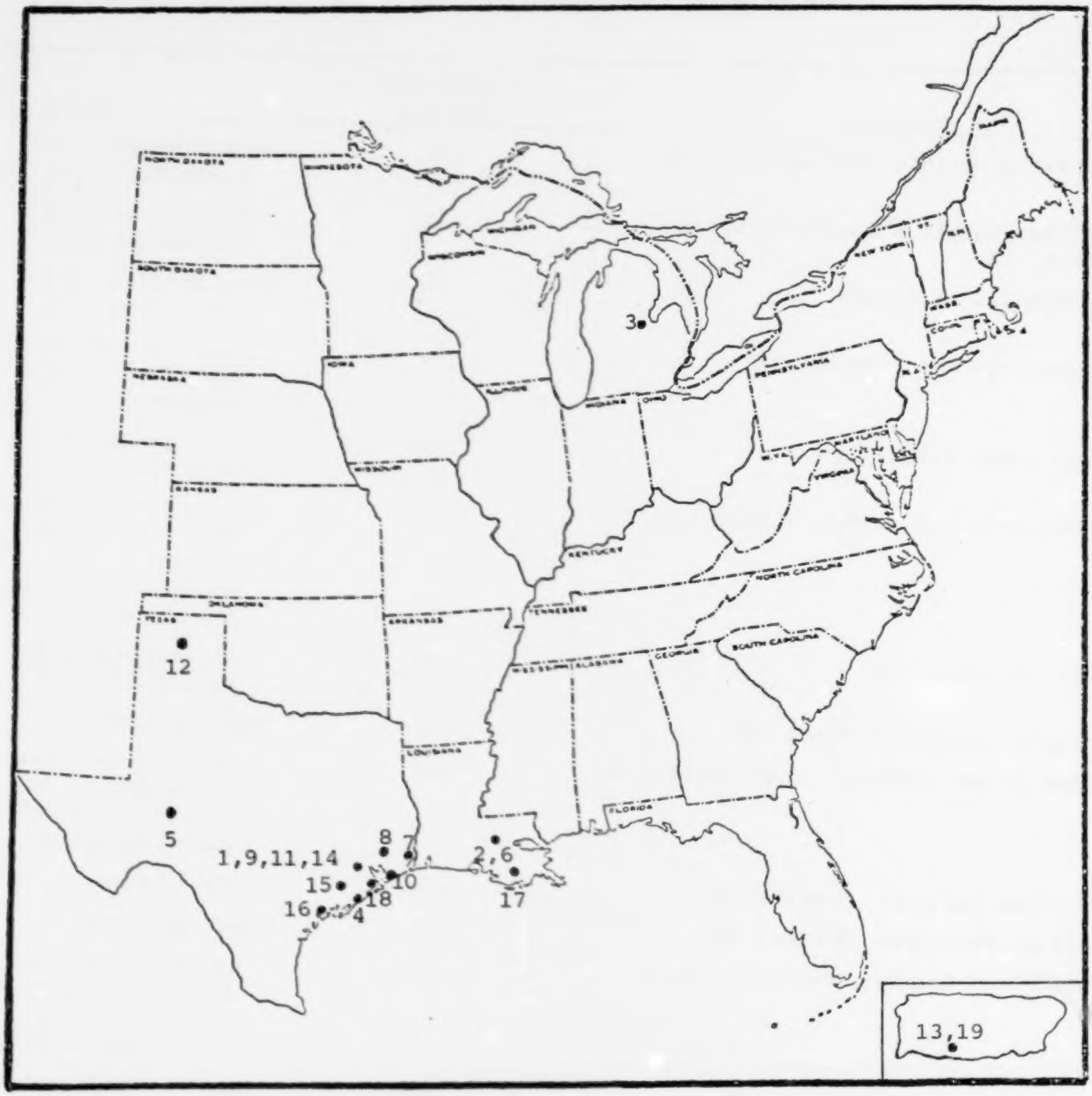
7. Mobil Corporation

Butadiene is extracted from ethylene plant by-product streams and sold.

Table II-3. Butadiene Capacity*

Producer	Capacity (Gg/yr)	Process
Atlantic Richfield, Channelview, TX	204	From ethylene plant by-product C_4's
Copolymer Rubber & Chemical, Baton Rouge, LA	73	n-Butenes oxidative dehydrogenation
Dow Chemical, Freeport, TX	39	From ethylene plant by-product C_4's
El Paso Products, Odessa, TX	91	By n-butane dehydrogenation (Houdry process)
Exxon, Baton Rouge, LA	154	From ethylene plant by-product C_4's
Firestone Tire & Rubber, Orange, TX	104	By n-butane dehydrogenation (Houdry process), n-butenes oxidative dehydrogenation
Mobil, Beaumont, TX	36	From ethylene plant by-product C_4's
Monsanto, Chocolate Bayou, TX	55	Same as above
Neches Butane Products, Port Neches, TX	363	From ethylene plant by-product C_4's n-butenes oxidative dehydrogenation
Petro-Tex Chemical, Houston, TX	>227	Same as above
Phillips Petroleum, Borger, TX	131	Same as above
Puerto Rico Olefins, Penuelas, PR		From ethylene plant by-product C_4's (operation discontinued in 1978)
Shell Chemical, Deer Park, TX	118	Same as above
Standard Oil (Indiana) Alvin, TX	82	Same as above
Union Carbide, Seadrift, TX	20	Same as above
Union Carbide, Taft, LA	25	Same as above
Union Carbide, Texas City, TX	30	Same as above
Union Carbide, Penuelas, PR	70	Same as above
	1821	

*See ref. 1.



1. Atlantic Richfield Co., Channelview, TX
2. Copolymer Rubber & Chemical Corp., Baton Rouge, LA
3. Dow Chemical Co., Bay City, MI*
4. Dow Chemical Co., Freeport, TX
5. El Paso Products Co., Odessa, TX
6. Exxon Chemical Co., Baton Rouge, LA
7. Firestone Tire & Rubber Co., Orange, TX
8. Mobil Chemical Co., Beaumont, TX
9. Monsanto Company, Chocolate Bayou, TX
10. Neches Butane Products Co., Port Neches, TX
11. Petro-Tex Chemical Corp., Houston, TX
12. Phillips Petroleum Co., Borger, TX
13. Puerto Rico Olefins Co., Penuelas, PR*
14. Shell Chemical Co., Deer Park, TX
15. Standard Oil Co., Alvin, TX
16. Union Carbide Corp., Seadrift, TX
17. Union Carbide Corp., Taft, LA
18. Union Carbide Corp., Texas City, T
19. Union Carbide Corp., Penuelas, P

*Operation discontinued.

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Fig. II-1. Locations of Plants Manufacturing Butadiene

8. Monsanto Company
   Butadiene is extracted from ethylene plant by-product streams. More than 95% is captively consumed for ABS resin manufacture at two domestic locations.

9. Neches Butane Products Company
   Butadiene is produced by the oxidative dehydrogenation of n-butenes and by extraction from ethylene plant by-product streams. Butadiene is consumed by B. F. Goodrich Company and Texas--U. S. Chemical Company (joint owners of Neches Butane Products Company) to produce SBR, polybutadiene, nitrile elastomers, ABS resins, and styrene-butadiene latex.

10. Petro-Tex Chemical Corporation
    Butadiene is extracted from ethylene plant by-product streams and produced by oxidative dehydrogenation of n-butenes. Until early 1977 butadiene was also produced from n-butane by the Houdry process. The butadiene product is sold.

11. Phillips Petroleum Company
    Butadiene is extracted from ethylene plant by-product streams. Butadiene is captively consumed to produce polybutadiene thermoplastic elastomers and K-Resin®.

12. Puerto Rico Olefins Company
    Butadiene is extracted from ethylene plant by-product streams and sold.

13. Shell Chemical Company
    Butadiene is extracted from ethylene plant by-product streams and is primarily sold (20% is captively consumed).

14. Standard Oil Company (Indiana)
    Butadiene is extracted from ethylene plant by-product streams and sold.

15. Union Carbide Corporation
    Butadiene is extracted from ethylene plant by-product streams and primarily sold.

D. REFERENCE*

1. S. L. Soder, "Butadiene," pp. 620.5021A—620.5024D in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (June 1977)

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

Butadiene is produced in the United States by the dehydrogenation of *n*-butane (Houdry process), by the oxidative dehydrogenation of *n*-butenes, and as a by-product of ethylene manufacture.[1] As the ethylene plant by-product streams containing butadiene also generally contain significant quantities of *n*-butane and *n*-butenes (see Table III-4 in Sect. D for typical composition), a number of producers currently utilize combined processes, extracting the contained butadiene and producing additional butadiene by dehydrogenation of contained *n*-butenes or *n*-butane.[2--5]

Most routes require final purification of butadiene by extraction or by extractive distillation. Five different butadiene extraction or extractive distillation processes are used commercially; each uses a different extraction solvent. The processes as identified by the company licenser and the type of solvent used are as follows:[1]

Nippon Zeon Co., Ltd. -- dimethyl formamide (DMF)
Phillips Petroleum Company -- furfural
Shell Chemical Company -- acetonitrile
Union Carbide Corporation -- dimethyl acetamide
(No licenser) -- cuprous ammonium acetate solution (CAA)

The production of butadiene by the dehydrogenation of *n*-butane and *n*-butenes has been steadily decreasing as a percentage of the total butadiene production since more butadiene has become available from ethylene plants. This trend will continue through 1983. By that time dehydrogenation processes are expected to be used for only 19 to 24% of the total domestic butadiene production.[1]

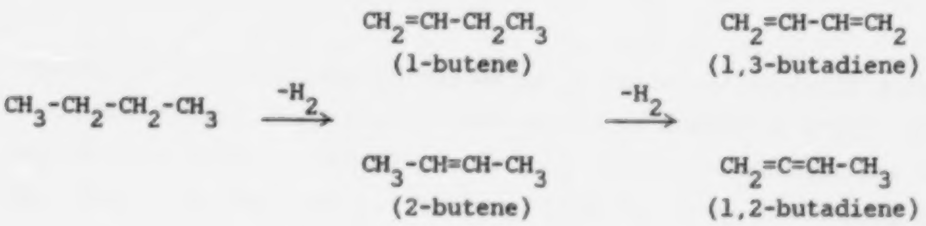
Historically, butadiene has also been produced in the United States from ethanol feedstock and as a by-product of petroleum coke production. Neither process is now being used in the United States.[1]

Virtually all butadiene production in Western Europe and Japan is based on ethylene by-product recovery. Houdry units (*n*-butane dehydrogenation) are currently operating in Argentina, Brazil, Mexico, and the USSR. The only *n*-butenes dehydrogenation unit outside the United States is located in Canada. Plants that produced butadiene from ethanol in India and in the People's Republic of China have reportedly been shut down.

B. HOUDRY PROCESS FOR DEHYDROGENATION OF n-BUTANE

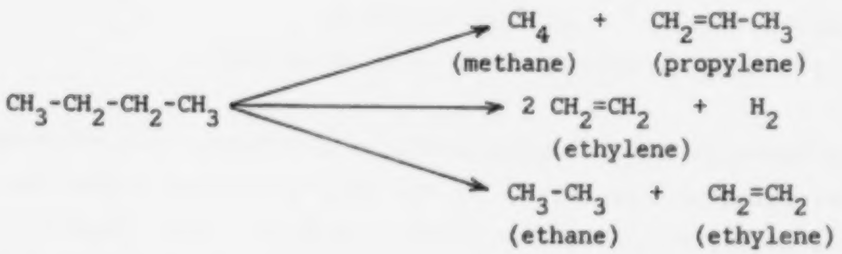
1. Basic Process

The dehydrogenation of n-butane proceeds through 1-butene and 2-butene to 1,3-butadiene and 1,2-butadiene:



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow{-H_2} \begin{matrix} CH_2\text{=}CH\text{-}CH_2CH_3 \\ \text{(1-butene)} \\ \\ CH_3\text{-}CH\text{=}CH\text{-}CH_3 \\ \text{(2-butene)} \end{matrix} \xrightarrow{-H_2} \begin{matrix} CH_2\text{=}CH\text{-}CH\text{=}CH_2 \\ \text{(1,3-butadiene)} \\ \\ CH_2\text{=}C\text{=}CH\text{-}CH_3 \\ \text{(1,2-butadiene)} \end{matrix}$$

The adjoining double bonds in 1,2-butadiene are unstable at elevated temperatures and thus 1,2-butadiene is formed only in trace amounts. Butane may also undergo various degradation reactions.[3]



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \rightarrow \begin{cases} \underset{\text{(methane)}}{CH_4} + \underset{\text{(propylene)}}{CH_2\text{=}CH\text{-}CH_3} \\ 2\ \underset{\text{(ethylene)}}{CH_2\text{=}CH_2} + H_2 \\ \underset{\text{(ethane)}}{CH_3\text{-}CH_3} + \underset{\text{(ethylene)}}{CH_2\text{=}CH_2} \end{cases}$$

Equilibrium constants for n-butane degradation to methane, ethane, ethylene, and propylene are larger than for its dehydrogenation, and a catalyst is essential for increasing the rate of dehydrogenation.[3]

Finally, acetylene compounds are formed either through recombination of radicals or by the dehydrogenation of propylene and butenes. Possible acetylenes are methylacetylene, ethylacetylene, dimethylacetylene, vinylacetylene, and diacetylene. These acetylenes are present in butane dehydrogenation products in only very small or trace quantities. However, because they interfere with the subsequent polymerization of butadiene and because their similarity to other C_4 hydrocarbons makes their separation difficult, even amounts as low as 100 ppm can be objectionable.[3]

Dehydrogenation of n-butane to butadiene in the Houdry process requires temperatures of about 600°C and an n-butane partial pressure of 15 to 35 kPa. The reaction takes place in a fixed-bed reactor over a chromia-alumina catalyst. Per-pass conversion is about 30%, with butylenes and unreacted butane being recycled for further reaction. Overall yields are reportedly 50 to 55%, requiring about 2 kg of butane per kg of butadiene produced. The typical composition of the reactor effluent, before product separation and purification, is shown in Table III-1.[3]

The process flow diagram in Fig. III-1 represents a typical n-butane dehydrogenation (Houdry) process.[2--5] Butane feed (Stream 1) and recycle butane and butenes (Stream 23) are combined and preheated to 600°C in a fuel-fired feed preheater and passed through three or four of seven parallel catalytic reactors (Stream 2) initially at a temperature of 650°C. The reaction is endothermic and the catalyst beds cool gradually. The seven reactors are operated on a cyclic basis, with three or four reactors being regenerated at all times. During the regeneration phase the reactors are first steam purged to the quench tower (steam purge is not shown) and then blown with air preheated to 650°C (Stream 3); as a result coke and deposited hydrocarbons from the catalyst beds are burned, thereby reheating the beds to 650°C. The reactors are evacuated before air regeneration and before being returned to service. The hot regeneration air containing a significant concentration of VOC is a primary emission source from the process (Stream 4) and is passed through a waste-heat-recovery boiler before it is vented to the atmosphere through an emission control device (Vent C). Flue gas from the feed preheater is formed from the combustion of gaseous fuels and is vented without control (Vents A).

The hot process gas from the reactors (Stream 5) (see Table III-1 for typical composition) is cooled to approximately 200°C in the oil quench tower. The quench oil is cooled (Stream 6) before recirculation. Following further cooling to approximately 50°C the process gas (Stream 7) is compressed to about 1.1 MPa.

Table III-1. Typical Composition of *n*-Butane Dehydrogenation (Houdry) Reactor Effluent (Fig. III-1, Stream 5)*

Component	Molecular Formula	Composition (wt %)
Hydrogen	H_2	1.4
Carbon oxides	CO, CO_2	0.7
Methane	CH_4	0.7
Ethane	C_2H_6	0.3
Ethylene	C_2H_4	0.6
Propane	C_3H_8	0.1
Propylene	C_3H_6	1.0
n-Butane	C_4H_{10}	40.5
Isobutane	C_4H_{10}	1.0
Isobutene	C_4H_8	4.3
1-Butene	C_4H_8	12.7
Trans-2-butene	C_4H_8	13.6
Cis-2-butene	C_4H_8	11.3
1,3-Butadiene	C_4H_6	11.1
C_5's hydrocarbons		0.6
1,2-Butadiene	C_4H_6	Trace
Propadiene	C_3H_4	Trace
Methylacetylene	C_3H_4	Trace
Ethylacetylene	C_4H_6	Trace
Dimethylacetylene	C_4H_6	Trace
Vinylacetylene	C_4H_4	Trace
		100.0

*See ref 3.

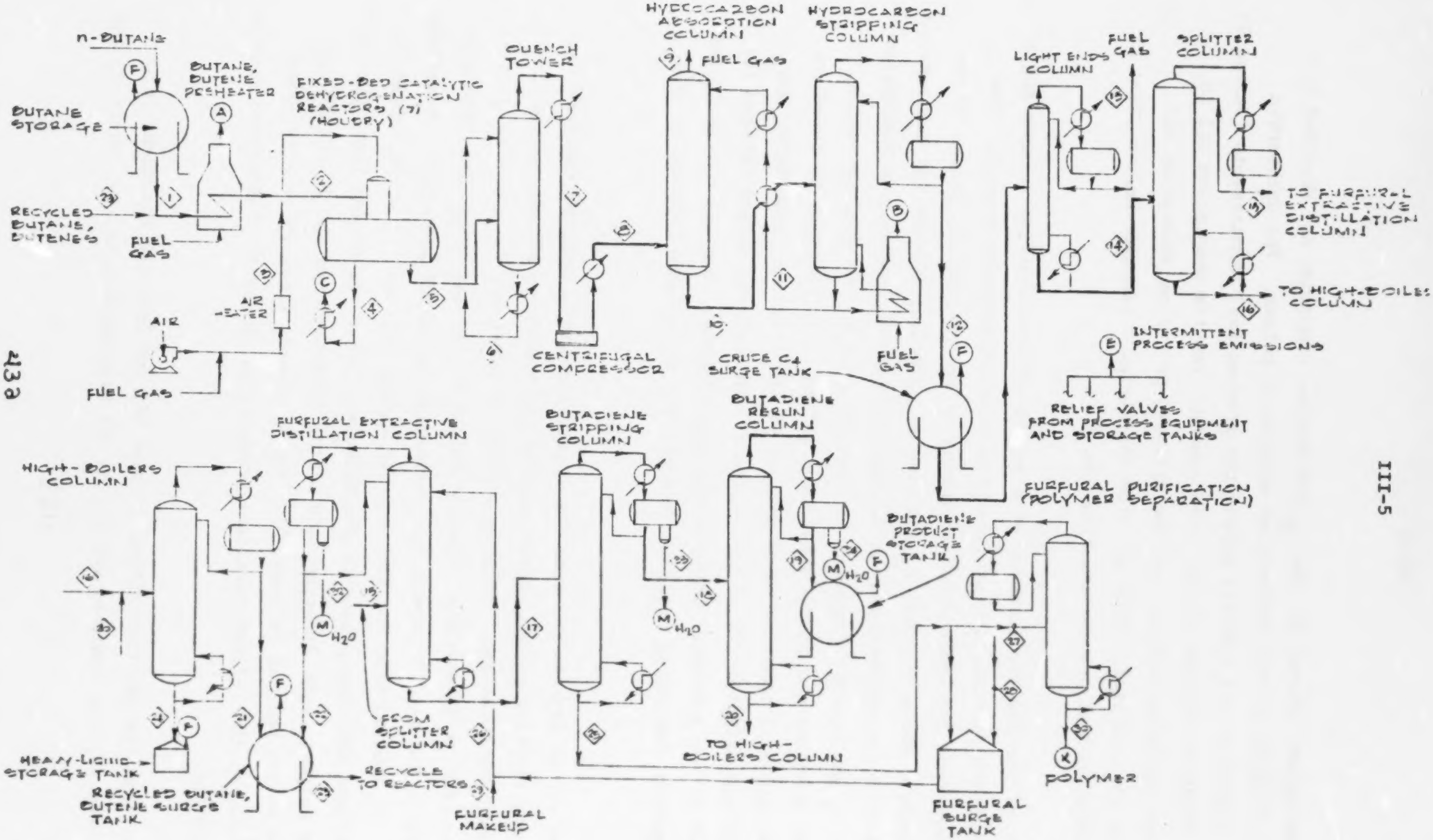

n-BUTANE
F
BUTANE STORAGE
BUTANE, BUTENE PREHEATER
A
RECYCLED BUTANE, BUTENES
23
1
FUEL GAS
FIXED-BED CATALYTIC DEHYDROGENATION REACTORS (7) (HOUDRY)
2
3
AIR HEATER
AIR
FUEL GAS
C
4
5
QUENCH TOWER
6
7
CENTRIFUGAL COMPRESSOR
8
HYDROCARBON ABSORPTION COLUMN
9
FUEL GAS
10
HYDROCARBON STRIPPING COLUMN
11
B
FUEL GAS
12
F
CRUDE C4 SURGE TANK
LIGHT ENDS COLUMN
FUEL GAS
13
14
SPLITTER COLUMN
15
TO FURFURAL EXTRACTIVE DISTILLATION COLUMN
16
TO HIGH-BOILERS COLUMN
E
INTERMITTENT PROCESS EMISSIONS
RELIEF VALVES FROM PROCESS EQUIPMENT AND STORAGE TANKS
HIGH-BOILERS COLUMN
16
30
24
K
HEAVY-LIQUID STORAGE TANK
F
21
22
RECYCLED BUTANE, BUTENE SURGE TANK
23
FURFURAL EXTRACTIVE DISTILLATION COLUMN
32
M
H_2O
15
FROM SPLITTER COLUMN
RECYCLE TO REACTORS
26
29
FURFURAL MAKEUP
17
BUTADIENE STRIPPING COLUMN
33
M
H_2O
18
25
BUTADIENE RERUN COLUMN
19
34
M
H_2O
F
20
TO HIGH-BOILERS COLUMN
BUTADIENE PRODUCT STORAGE TANK
FURFURAL PURIFICATION (POLYMER SEPARATION)
27
28
25
K
POLYMER
FURFURAL SURGE TANK

Fig. III-1. Flow Diagram of Uncontrolled Model Plant for Production of Butadiene by n-Butane Dehydrogenation (Houdry) Process

Following compression (Stream 8), the C_4 and heavier compounds are absorbed in a petroleum oil fraction in the hydrocarbon absorption column. The unabsorbed "lights" (C_3 compounds and lighter) supply the process fuel requirements (Stream 9). The absorbed organics (Stream 10) are then removed from the absorption oil in the hydrocarbon stripping column, and the stripped petroleum absorption oil (Stream 11) is recirculated. Flue gas from the stripper reboiler heater (Vent B) is the only other normal process emission source.

The remainder of the process consists of a series of fractionation columns and a furfural extractive distillation section with no point emission sources. The overhead stream from the hydrocarbon stripping column (Stream 12) passes to the light-ends column, where residual C_3 and lighter compounds (Stream 13) are removed and combined with the overhead stream (Stream 9) from the hydrocarbon absorption column. The C_4 and heavier compounds (Stream 14) pass to the splitter column, where a rough n-butane--butadiene separation is made. In addition to butadiene the overhead stream (Stream 15) contains most of the 1-butene, isobutene, and isobutane and approximately 5% of the n-butane. The bottoms stream (Stream 16) contains most of the n-butane, trans-2- and cis-2-butenes, and all of the C_5 and heavier compounds (including residual absorber oil and polymers formed in the process).

The overhead stream (Stream 15) from the splitter column passes to the furfural extractive distillation column, where most of the remaining butanes and butenes are separated from butadiene. This separation is difficult to attain by distillation alone (due to unfavorable relative volatilities) and extractive distillation techniques are used in almost all commercial butadiene processes. Butadiene (Stream 18) is removed from the rich solvent stream (Stream 17) in the butadiene stripping column and then passes to the butadiene rerun column for final purification, where polymer, some 2-butene, and traces of acetylenes and 1,2-butadiene are removed in the bottoms (Stream 20). The overhead stream (Stream 19) from the rerun column, the refined butadiene product, is stored in pressurized spheres for distribution.

The bottoms from the splitter column (Stream 16) and from the butadiene rerun column (Stream 20) are combined and fed to the high-boilers column, where C_5 and heavier components, polymer, and residual absorber oil are separated. The bottoms fraction (Stream 24) may be used as fuel or further separated into other product fractions.

The overhead streams from the high-boilers column (Stream 21) and from the extractive distillation column (Stream 22) are composed of butanes and butenes and are combined and recycled to the dehydrogenation reactor (Stream 23). After the stripped furfural solvent from the butadiene stripping column (Stream 25) is cooled, most of it is recycled to the butadiene extractive distillation column (Stream 26).

A small portion of the circulating furfural solvent (Stream 27) is continuously processed in the furfural purification column to remove accumulated polymer, with the purified furfural (Stream 28) being returned to the cycle. Furfural makeup (Stream 29) is introduced as necessary to compensate for losses from the cycle. Polymer removed by the furfural purification column (Stream 30) is discharged as a waste stream (Source K).

Water is phase separated from the condensed overhead streams from the extractive distillation column (Stream 32), the butadiene stripping column (Stream 33), and the butadiene rerun column (Stream 34) and discharged as wastewater (Source M).

2. Process Variations[2]

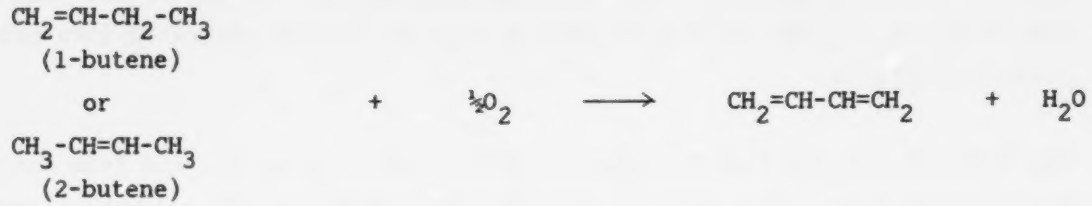
The primary process variations are in the solvent systems used in the extraction or extractive distillation sections. Furfural, acetonitrile, and cuprous ammonium acetate solution (CAA) are used in the current *n*-butane dehydrogenation processes and in those in stand-by status. The use of alternate solvent systems results in a number of corresponding variations in purification and solvent recovery steps that may significantly affect process emissions.

The recycle feed stream (Stream 23) may be processed to either remove butenes or to convert them to butanes before it is recycled.

C. OXIDATIVE DEHYDROGENATION OF *n*-BUTENES

1. Basic Process

The oxidative dehydrogenation of *n*-butenes (1- and 2-butenes) proceeds through the following primary reaction:[3]



$$\begin{array}{c} CH_2{=}CH{-}CH_2{-}CH_3 \\ \text{(1-butene)} \\ \text{or} \\ CH_3{-}CH{=}CH{-}CH_3 \\ \text{(2-butene)} \end{array} + \tfrac{1}{2}O_2 \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2O$$

Per-pass conversions of 75 to 85% and overall yields of 80 to 90% are obtained; this corresponds to consumption of 1.1 to 1.3 kg of n-butenes per kg of butadiene formed. With higher product yields the quantities of degradation products formed are correspondingly less than from the butane dehydrogenation process.[3]

The process flow diagram in Fig. III-2 represents a typical n-butene oxidative dehydrogenation process.[2,3,5] n-Butene feed (Stream 1), recycle butenes (Stream 23), and steam (Stream 3) are preheated in fuel-fired preheaters and mixed with compressed air (Stream 2). The combined stream (Stream 4) is passed through fixed-bed catalytic reactors at 500 to 550°C. One catalyst system that is used is a mixture of oxides of tin, bismuth, and boron, with phosphoric acid. The reaction is exothermic and the reactors are operated continuously.

A typical composition of the reactor effluent (Stream 5) is shown in Table III-2. Although the remaining process is similar to the corresponding portion of the Houdry process, significant differences in reactor effluent composition result in the following differences in downstream process conditions and requirements:

a. Significant quantities of water (resulting from the introduction of steam and from the formation of water in the reaction) are present. The water, which is removed before compression, results in the generation of additional wastewater (Streams 6 and 7).

b. Air (nitrogen and excess oxygen) is removed from the process stream by the hydrocarbon absorption column and vented (Stream 9) to an emission control device (Vent D). Fuel gas components (C_3 compounds and lighter) are present in relatively low concentrations.

c. The quantity of recycle feed (Stream 23) is less than that from the Houdry process because of the more complete conversion per pass attained.

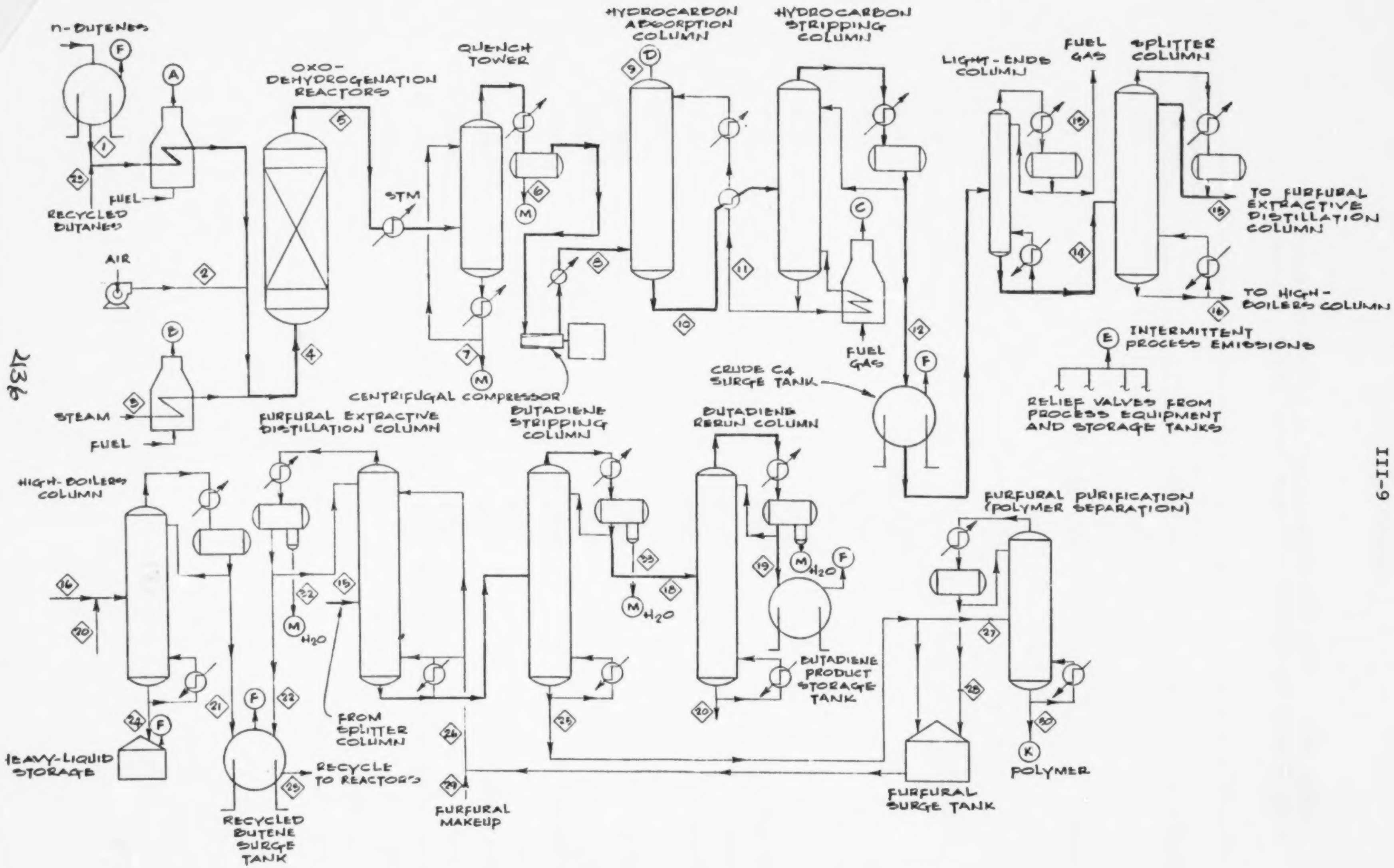

n-BUTENES
F
A
RECYCLED BUTANES
FUEL
AIR
STEAM
FUEL
B
OXO-DEHYDROGENATION REACTORS
STM
QUENCH TOWER
M
CENTRIFUGAL COMPRESSOR
HYDROCARBON ABSORPTION COLUMN
D
HYDROCARBON STRIPPING COLUMN
C
FUEL GAS
CRUDE C4 SURGE TANK
LIGHT-ENDS COLUMN
FUEL GAS
SPLITTER COLUMN
TO FURFURAL EXTRACTIVE DISTILLATION COLUMN
TO HIGH-BOILERS COLUMN
E
INTERMITTENT PROCESS EMISSIONS
RELIEF VALVES FROM PROCESS EQUIPMENT AND STORAGE TANKS
FURFURAL EXTRACTIVE DISTILLATION COLUMN
BUTADIENE STRIPPING COLUMN
BUTADIENE RERUN COLUMN
HIGH-BOILERS COLUMN
HEAVY-LIQUID STORAGE
RECYCLED BUTENE SURGE TANK
RECYCLE TO REACTORS
FROM SPLITTER COLUMN
FURFURAL MAKEUP
H2O
BUTADIENE PRODUCT STORAGE TANK
FURFURAL PURIFICATION (POLYMER SEPARATION)
FURFURAL SURGE TANK
K
POLYMER

Fig. III-2. Flow Diagram of Uncontrolled Model Plant for Production of n-Butenes Oxidative Dehydrogenation Process

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Table III-2. Typical Composition of _n_-Butene Oxidative Dehydrogenation Reactor Effluent (Fig. III-2, Stream 5)*

Component	Molecular Formula	Composition (wt %)
Oxygen	O_2	1.0
Nitrogen	N_2	15.8
Carbon oxides	CO, CO_2	3.0
Water	H_2O	65.0
Methane	CH_4	0.1
C_2's		0.3
C_3's		0.4
_n_-Butane	C_4H_{10}	0.4
Isobutane	C_4H_{10}	0.6
Isobutene	C_4H_8	1.1
1-Butene	C_4H_8	1.9
Trans-2-butene	C_4H_8	1.7
Cis-2-butene	C_4H_8	1.4
1,3-Butadiene	C_4H_6	7.2
C_5's		0.1
1,2-Butadiene	C_4H_6	Trace
Propadiene	C_3H_4	Trace
Methylacetylene	C_3H_4	Trace
Ethylacetylene	C_3H_4	Trace
Dimethylacetylene	C_4H_6	Trace
Vinylacetylene	C_4H_4	Trace

*See ref 3.

The remaining process steps are essentially the same as the corresponding steps in the Houdry process, and identical stream designations are used.

2. Process Variations[2]

The alternative extractive distillation solvents listed in Sect. III-A may be used.

With smaller quantities of butenes and very little butane present a splitter column may be omitted. In this case the recycled butenes are separated from butadiene by the extractive distillation column.

The recycle stream (Stream 23) may be further processed to remove isobutene and butanes, with only n-butenes recycled to the process.

D. EXTRACTION FROM ETHYLENE PLANT BY-PRODUCT STREAMS

1. Basic Process

The amount of butadiene produced during ethylene manufacture is dependent on both the type of feedstock and the severity of the cracking operation.[6] Table III-3 summarizes typical butadiene yields from ethylene production based on various feedstocks. The increasing use of heavy feedstocks (naphthas and gas oils) for ethylene production has resulted in the production of much larger quantities of butadiene from this source. A typical composition of a C_4 by-product stream from an ethylene plant using naphtha feedstocks is shown in Table III-4. The process is similar to the separation/purification portions of the dehydrogenation processes discussed in Sects. III-B and C; however, the following significant differences, resulting from differences in composition (see Tables III-1 and III-4), are noted:

a. Because almost all the components heavier or lighter than C_4 compounds have been removed by the ethylene plant fractionation columns, further separation of these components is not required in the butadiene process.
b. Because the concentrations of acetylenes (methylacetylene, dimethylacetylene, vinylacetylene, ethylacetylene) present in the C_4 streams are much higher than those formed in the dehydrogenation processes, more extensive provisions for acetylene removal are required.

Table III-3. Butadiene By-Product Yields from Ethylene Production Based on Various Feedstocks[a]

Feed	Yield Ratio[b] (kg/100 kg)
Ethane	1.0--2.0
Refinery off-gas	5.0
Propane	5.0--8.5
n-Butane	7.0--8.5
Naphthas	13.0--18.0
Gas oils	17.6--24.7

[a] See ref. 1.

[b] kg of butadiene per 100 kg of ethylene produced.

Table III-4. Typical Composition of Ethylene Plant C_4 By-Product Stream from Naphtha Feedstock*

Component	Molecular Formula	Composition (wt %)
n-Butane	C_4H_{10}	6.8
Isobutane	C_4H_{10}	1.6
Isobutene	C_4H_8	29.0
1-Butene	C_4H_8	9.6
Trans-2-butene	C_4H_8	7.5
Cis-2-butene	C_4H_8	4.7
1,3-Butadiene	C_4H_6	39.3
1,2-Butadiene	C_4H_6	0.08
Propadiene	C_3H_4	0.53
Methyl acetylene	C_3H_4	0.65
Ethyl acetylene	C_4H_6	0.05
Dimethyl acetylene	C_4H_6	0.08
Vinyl acetylene	C_4H_4	0.11
		100.0

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*See ref. 3.

Referring to Fig. III-3, the C_4 feed (Stream 1) and hydrogen (Stream 2) are combined and passed through a fixed-bed hydrogenation reactor, where approximately 95% of the contained acetylenes are converted to olefins. Typical hydrogenation conditions include a metal oxide catalyst, a temperature of 60 to 70°C, and a pressure of about 800 kPa. The catalyst must be periodically regenerated (approximately 4 times per year) by preheated air and steam (Stream 3) being passed over the catalyst bed, effectively burning the deposited organics. During regeneration the reactor effluent is vented (Vent A). Combustion products from fuel gas burned in the regeneration heat furnace are also vented (Vent B) during regeneration.

Following hydrogenation the C_4 stream passes to the extractive distillation column, where most of the butanes and butenes are separated from butadiene. The butane-butene overhead stream from the extractive distillation column (Stream 5) is transferred to storage. This stream may be removed as a by-product stream or be converted to additional butadiene by dehydrogenation. Butadiene and residual impurities are removed from the rich solvent (Stream 6) in the butadiene stripping column and pass (Stream 7) to the methylacetylene column, where most of the residual acetylenes not converted in the acetylene hydrogenation reactors are vented (Source C) to an emission control device.

The bottoms stream from the methylacetylene column (Stream 9) is given a final purification by the butadiene rerun column, where polymer, some 2-butene, and traces of acetylene and 1,2-butadiene are removed as a residue stream (Source L).

Most of the stripped furfural solvent from the butadiene stripping column (Stream 10) is recycled to the extractive distillation column (Stream 11). A small portion of the circulating furfural solvent (Stream 12) is continuously processed in the furfural purification column for removal of accumulated polymer, with the purified furfural (Stream 13) being returned to the cycle. Furfural makeup (Stream 14) is introduced as necessary to compensate for losses from the cycle. Polymer removed by the furfural purification column (Stream 15) is discharged as a process waste stream (Source K).

Water is phase separated from the condensed overhead streams from the extractive distillation column (Stream 16), the butadiene stripping column (Stream 17), the methylacetylene column (Stream 18), and the butadiene rerun column (Stream 19) and is discharged as wastewater (Source M).

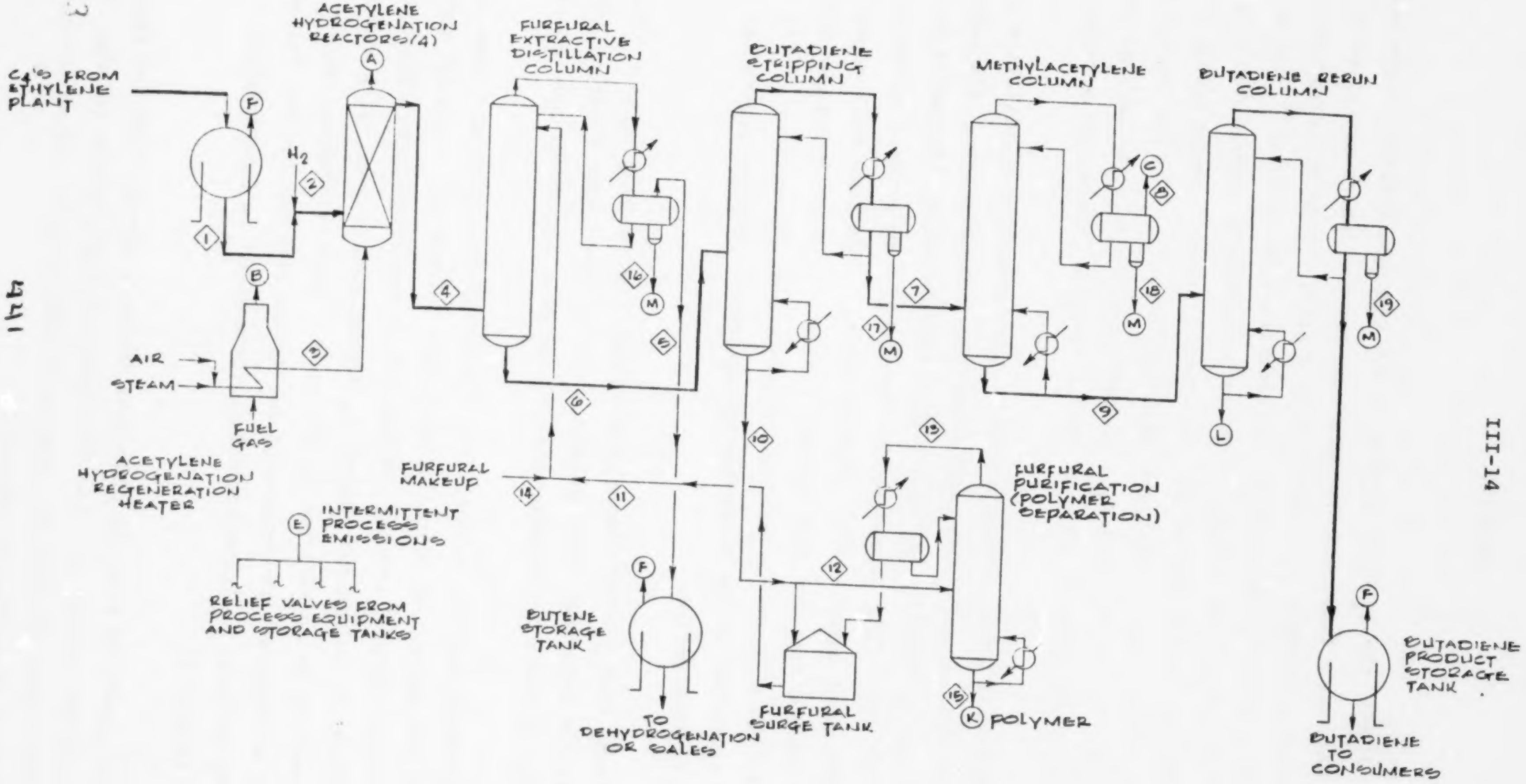
C4'S FROM ETHYLENE PLANT
F
1
H2
2
ACETYLENE HYDROGENATION REACTORS(4)
A
B
AIR
STEAM
3
FUEL GAS
ACETYLENE HYDROGENATION REGENERATION HEATER
4
FURFURAL EXTRACTIVE DISTILLATION COLUMN
16
M
5
6
FURFURAL MAKEUP
14
11
E
INTERMITTENT PROCESS EMISSIONS
RELIEF VALVES FROM PROCESS EQUIPMENT AND STORAGE TANKS
F
BUTENE STORAGE TANK
TO DEHYDROGENATION OR SALES
BUTADIENE STRIPPING COLUMN
17
M
7
10
12
FURFURAL SURGE TANK
13
FURFURAL PURIFICATION (POLYMER SEPARATION)
15
K
POLYMER
METHYLACETYLENE COLUMN
C
8
18
M
9
BUTADIENE RERUN COLUMN
19
M
L
F
BUTADIENE PRODUCT STORAGE TANK
BUTADIENE TO CONSUMERS

Fig. III-3. Flow Diagram for the Extraction of Butadiene from Ethylene Plant By-Product Streams

2. Process Variations

The alternative extraction or extractive distillation solvents listed in Sect. III-A may be used. Emissions from processes using other solvent systems may differ from those estimated for the model plant.

The contained acetylenes may be removed by solvent extraction and/or extractive distillation instead of primarily by catalytic hydrogenation to olefins. The separated acetylenes are generally burned as supplementary boiler fuel or in flares.

E. REFERENCES*

1. S. L. Soder, "Butadiene," pp. 620.5021A--620.5024D in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (June 1977).

2. Texas Air Control Board, 1975 Emission Inventory Questionnaires; see Appendix C.

3. G. E. Haddeland, Butadiene, Report No. 35, A private report by Process Economics Program, Stanford Research Institute, Menlo Park, CA (March 1968); see also G. E. Haddeland, Report No. 35A1 (March 1972).

4. R. L. Standifer, IT Enviroscience, Inc., Trip Report for Visit to Arco Chemical Company, Channelview, TX, August 16, 17, 1977 (data on file at EPA, ESED, Research Triangle Park, NC).

5. R. L. Standifer, IT Enviroscience, Inc., Trip Report for Visit to Petro-Tex Chemical Corp., Houston, TX, October 18, 1977 (data on file at EPA, ESED, Research Triangle Park, NC).

6. R. L. Standifer, IT Enviroscience, Inc., Ethylene (Olefins) (in preparation for EPA, ESED, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS AND APPLICABLE CONTROL SYSTEMS

A. GENERAL

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern ans may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

Current domestic butadiene is produced by n-butane dehydrogenation (Houdry process), by the oxidative dehydrogenation of n-butenes, and by extraction from ethylene plant by-product streams. With more of the generally lower cost butadiene from ethylene plant by-product streams becoming available as more heavy-liquid feedstocks are used for ethylene production, almost all new butadiene production is expected to be from this source. Concurrently the resulting excess dehydrogenation capacity will be converted for extraction of by-product butadiene, be placed in standby status for surge capacity, or be retired.

Estimated ratios (kg of VOC emissions/Mg of butadiene produced) of uncontrolled and controlled VOC (volatile organic compounds) emissions for the three processes described in Sects. III-B, C, and D are summarized in Tables IV-1 through IV-3.

The estimates of uncontrolled emissions from normal process vents are based on a compilation of data from existing sources.[1--3] The corresponding estimates of controlled emissions from normal process vents are based on the efficiencies reported for control devices used in the butadiene industry[2--4] or for similar applications in other process industries.

Storage and handling emissions for all three of the processes shown are approximately the same. The estimated emission ratios, which are relatively low, are based on the use of pressurized tanks for the storage of feedstocks, intermediates, and primary products. The recycle of vapor vented from storage tanks and transfer operations is common in the industry and is considered to be a normal process feature.

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Table IV-1. Uncontrolled and Controlled VOC Emissions from Butadiene Production by Dehydrogenation of n-Butane (Houdry Process)

Source	Stream Designation (Fig. III-2)	Uncontrolled-Emission Ratio (kg/Mg)[a]	Control Device or Technique	Emission Reduction (%)	Controlled-Emission Ratio (kg/Mg)[a]
Flue gas	A,B	0.06	None		0.06
Reactor vent (regeneration air)	C	5.5	Catalytic or thermal oxidation	92	0.44
Intermittent process emissions	E	0.5	Elevated flare	95	0.03
Storage and handling	F	0.1	None[b]		0.1
Secondary	K,M	0.15	None		0.15
Fugitive		5.2	Detection and repair of major leaks plus mechanical seals	90	1.3
Total		11.5			2.1

[a] kg of VOC per Mg of butadiene produced.

[b] Pressurized storage tanks vented to the process are considered to be normal process conditions, not a separate emission control.

Table IV-2. Uncontrolled and Controlled VOC Emissions from Butadiene Production by Oxidative Dehydrogenation of n-Butenes

Source	Stream Designation (Fig. III-2)	Uncontrolled-Emission Ratio (kg/Mg)[a]	Control Device or Technique	Emission Reduction %	Controlled-Emission Ratio (kg/Mg)[a]
Flue Gas	A,B,C	0.06	None		0.06
Absorption column vent	D	5.0	Catalytic or thermal oxidation	95	0.25
Intermittent process emissions	E	0.5	Elevated flare	95	0.03
Storage and handling	F	0.1	None[b]		0.1
Secondary	k,m	0.75	Reactor wastewater stripper-flare vented vapor	70	0.24
Fugitive		5.2	Detection and repair of major leaks plus mechanical seals	90	0.13
Total		11.6			2.0

[a] kg of VOC per Mg of butadiene produced.

[b] Pressurized storage tanks vented to the process are considered a normal process condition, not a separate emission control.

Table IV-3. Uncontrolled and Controlled VOC Emissions from Butadiene Production by Extraction from Ethylene Plant By-Product Streams

Source	Stream Designation (Fig. III-3)	Uncontrolled-Emission Ratio (kg/Mg)[a]	Control Device or Technique	Emission Reduction (%)	Controlled-Emission Ratio (kg/Mg)[a]
Flue gas	A	0.002	None		0.002
Hydrogenation catalyst regeneration vent	B	0.024	None		0.024
Methylacetylene column vent	C	2.1	Incineration or flare	95	0.10
Intermittent process emissions	E	0.25	Elevated flare	95	0.015
Storage and handling	F	0.1	None[b]		0.10
Secondary	K,M	0.15	None		0.15
Fugitive		2.5	Detection and repair of major leaks plus mechanical seals	90	0.6
Total		5.1			1.0

[a] kg of VOC per Mg of butadiene produced.

[b] Pressurized storage tanks vented to the process are considered normal process conditions, not a separate emission control.

Estimates of potential fugitive emission sources are based on data from existing facilities. The estimated emission rates were calculated, with the emission factors shown in Appendix B, for plants annually producing 160 Gg of butadiene. As with most organic chemical processes, leaks into cooling water can occur, allowing VOC to escape.

Secondary emissions from wastewater (Source M) were estimated from reported wastewater rates and the corresponding organic concentrations. Significant quantities of process residues (polymers) are generated (Source K) and are normally diposed of by incineration or by landfill, with relatively low emissions of VOC.

Miscellaneous intermittent emissions (Source E) include emissions resulting from the activation of pressure-relief devices on storage tanks and process equipment and other emissions occurring during startups, shutdowns, and abnormal situations. Although average emissions from these sources are relatively low, abnormal situations can result in high emission rates for relatively short periods of time. Emissions from these sources are usually controlled by an elevated flare equipped with steam injection to provide mixing for improved combustion and smoke-free operation.

Emission sources and the corresponding emission control devices that apply specifically to the individual processes (i.e., n-butane dehydrogenation, oxidative dehydrogenation, extraction from ethylene plant by-product streams) are discussed in Sects. IV-B, C, and D.

B. DEHYDROGENATION OF n-BUTANE (HOUDRY PROCESS) (FIG. III-1, TABLE IV-1)

The normal process emissions occur from the following sources:

1. Flue Gas (Vents A, B, and C)

Emissions are composed of products generated from the combustion of primarily gaseous fuels. VOC concentrations are relatively low and the application of specific emission control devices is not indicated.

2. Dehydrogenation Reactor Vent (Vent D)

Emissions occur during the regeneration phase of the reactor cycle while the effluent regeneration air is being vented. Although the average VOC concentration in the vented regeneration air is relatively low (approximately 0.005 wt %), the extremely large quantity of vented air results in significant VOC emissions.

Emissions can be effectively controlled by thermal or catalytic oxidation. One manufacturer using a proprietary catalytic oxidation process reports a VOC destruction efficiency of 92% without the addition of auxiliary fuel, attaining an energy recovery efficiency of 80% from the combustion gas.

A catalytic oxidation system that processes the entire regeneration air stream reportedly attains a VOC removal efficiency of approximately 50%.

Thermal oxidation is a potential alternative control method, possibly providing higher VOC removal efficiencies than the catalytic oxidation systems described. However, with the relatively low concentrations of VOC in the regeneration air effluent streams, large quantities of auxiliary fuel would be required, with corresponding requirements for efficient energy recovery.

C. OXIDATIVE DEHYDROGENATION OF n-BUTENES (FIG. III-2, TABLE IV-2)

1. Normal Process Emissions

a. Flue Gas (Vents A, B, and C) -- Emissions are composed of products generated from the combustion of primarily gaseous fuels. VOC concentrations are relatively low and the application of specific emission control devices is not indicated.

b. Hydrocarbon Absorption Column Vent (Vent D) -- This stream, characterized by relatively low VOC concentrations but a very high flow rate, which results in significant VOC emissions, can be effectively controlled by catalytic or thermal oxidation. One producer[4] utilizes a thermal oxidizer to control this stream. The oxidizer is designed to treat 100 Mg of waste gas per hour and simultaneously generate 45 Mg of steam per hour at a pressure of 5.2 MPa. With the VOC content of the waste gas supplying 16% of the firing energy, 84% is provided by supplementary natural-gas fuel.

2. Secondary Emissions

a. Wastewater -- Potential secondary emissions from wastewater are significantly greater from the oxidative dehydrogenation process than from the other processes described. Wastewater, which is generated from steam addition and from water formed in the reaction, is removed from the process gas before compression (Source M, Stream 7). Wastewater from this source contains significant quantities of VOC. One producer[1] utilizes a stripper designed to attain 85% removal of the contained organics by countercurrent stripping with a portion of the waste gas described in Sect. C-1-b. The effluent gas from the stripper, containing the removed organics, is then combined with other waste gas prior to thermal oxidation.[1]

b. Solid Wastes -- Polymeric residues are disposed of by landfill or incineration. No specific additional controls are indicated.

D. EXTRACTION FROM ETHYLENE PLANT BY-PRODUCT STREAMS

The normal process emissions occur from the following sources:

1. Catalyst Regeneration Vents (Vents A and B)

Concentration of VOC emitted from the hydrogenation reactor during catalyst regeneration (Vent B) and from the flue-gas vent from the regeneration preheater (Vent A) is relatively low and occurs infrequently (approximately 4 times per year). No specific emission control devices are indicated.

2. Methylacetylene Column Vent (Vent C).

Most of the residual acetylenes (not converted by hydrogenation), along with significant quantities of butadiene, are vented as a waste stream. Emissions from this source can be effectively controlled by combustion, either in the flare system or in an existing combustion chamber. A VOC removal efficiency of 95% is considered to be attainable with the flare. If this stream is burned in a combustion chamber, a removal efficiency of at least 99% is attainable. Flare and incineration control efficiencies will be covered by a future EPA report on control device evaluations.

E. REFERENCES*

1. Texas Air Control Board, 1975 Emission Inventory Questionnaires and Construction Permit Application; see Appendix C.
2. R. L. Standifer, IT Enviroscience, Inc., Trip Report for Visit to Arco Chemical Company, Channelview, TX, Aug. 16, 17, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
3. R. L. Standifer, IT Enviroscience, Inc., Trip Report for Visit to Petro-Tex Chemical Corp., Houston, TX, Oct. 18, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
4. R. D. Pruessner, Hydrocarbon Emission Reduction Systems Utilized by Petro-Tex, presented at American Institute of Chemical Engineers 83rd National Meeting, 9th Petrochemical and Refining Exposition, Houston, TX, March 1977.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX A

Table A-1. Physical Properties of 1,3-Butadiene*

Property	Value
Molecular weight	54.092
Boiling point at 1 atm	24.06°F
Freezing point at 1 atm	-164.05°F
Specific gravity, liquid at 68°F/4°F	0.623
Specific gravity, gas (air = 1.0)	1.877
Critical temperature	305.6°F
Critical pressure	42.7 atm
Critical density	0.245 g/cc
Latent heat of vaporization at boiling point	179.6 Btu/lb
Vapor pressure	
At 50°F	25 psia
At 75°F	40 psia
At 100°F	60 psia
At 125°F	86 psia
Specific heat at 100°F	
Liquid	0.58 Btu/(lb)(°F)
Gas at 1 atm	0.36 Btu/(lb)(°F)
Solubility in water at 100°F and 50 psia	0.14 wt %
Solubility of water in butadiene at 60°F	0.203 wt %

Azeotropes	Boiling Point (°F)	Butadiene (wt %)
Ammonia	-35	45.0
Methylamine	+15	58.6
Acetaldehyde	+41	94.8
2-Butene	+42	76.5
n-Butane	Min. bp	

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*G. E. Haddeland, Butadiene, Report No. 35, A private report by the Process Economics Program, p. 238, Stanford Research Institute, Menlo Park, CA (March 1968).

APPENDIX B

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX C

1975 Texas Air Control Board Emission Inventory Questionnaires submitted by butadiene producers:

Atlantic Richfield Co., Channelview, TX
Dow Chemical Co., Freeport, TX
El Paso Products Co., Odessa, TX
Firestone Tire & Rubber Co., Orange, TX
Mobil Corp., Beaumont, TX
Neches Butane Products Co., Port Neches, TX
Petro-Tex Chemical Co., Port Neches, TX
Phillips Petroleum Co., Borger, TX
Shell Chemical Co., Deer Park, TX
Standard Oil Co. (Indiana), Alvin, TX
Union Carbide Corp., Seadrift, TX
Union Carbide Corp., Texas City, TX

APPENDIX D

EXISTING PLANT CONSIDERATIONS

A. CONTROL DEVICES

Table D-1 lists process control devices reported to be in use by industry. To gather information for the preparation of this report two site visits were made to manufacturers of butadiene. Trip reports have been cleared by the companies concerned and are on file at EPA, ESED, in Durham, NC. Additional information was received form other butadiene manufacturers when the original draft of this report was submitted to them for comments. Some of the pertinent information from those existing butadiene manufacturers is presented in this appendix.

1. Petro-Tex Chemical Corp. - Houston, TX

Butadiene is currently produced by extraction from ethylene plant by-product streams and by the oxidative dehydrogenation of n-butenes. Until early 1977 butadiene was also produced from n-butane by the Houdry process. Purification is attained by extractive distillation, with furfural used as the extraction solvent.

The primary process emissions from the oxidative dehydrogenation process are from the absorber column vent and the gas turbine exhaust. These emissions are controlled by an incinerator designed to treat 235,000-lb/hr waste gas containing about 4000-ppm organics and 7000-ppm carbon monoxide. The installed capital cost of the incineration system is $2.5 million (1976 dollars). This incinerator utilizes flue-gas recirculation, which permits steam generation at a constant rate of 100,000 lb/hr under conditions of widely varying waste-gas flow rates. (The waste-gas flow can range from 10% to 100% of the design production rate, with the corresponding auxiliary fuel consumed as needed to maintain a constant steam production rate.)

Prior to the shutdown of the Houdry butane dehydrogenation process by Petro-Tex in 1977, the dehydrogenation reactor vent (the primary Houdry process emission source) was controlled by a proprietary catalytic oxidation process. The oxidation reactors (termed "Puff" reactors by Petro-Tex) attained a VOC destruction efficiency of 92% without the addition of auxiliary fuel and attained an energy recovery efficiency of 80% from the combustion gas. With this process only 1%

Table D-1. Control Devices Used by Butadiene Producers

		Emission Source			
		Houdry Process	Oxo Process	Purification Section	
Company	Process	Reactor Vent	Absorber Vent	Acetylenes[a]	Other Process Vents
Arco Chemical Co.	Houdry[b]	Catalytic oxidizer			Flare[c]
	By-product extraction			Catalytic dehydrogenation	
Firestone Synthetic Rubber and Latex Co.	Houdry	Thermal oxidizer			NR[d]
	Oxo		Uncontrolled		
El Paso Products Co.	Houdry	Uncontrolled			NR
Exxon Chemical Co.	By-product extraction			Combustion in boiler	Flare[e]
Monsanto Chemical Co.	By-product extraction			Catalytic dehydrogenation (regeneration off-gas incinerated)	Flare, recycle to ethylene plant
Petro-Tex Chemical Corp.	Houdry[f]	Catalytic oxidizer			Flare
	Oxo		Thermal oxidizer		
	By-product extraction			NR	

---

[a] Methylacetylene and vinylacetylene. Quantities are significant only in ethylene plant by-product C_4's.

[b] Arco's Houdry units have been shut down.

[c] Tower relief valves vented without controls. All others vented to flare system.

[d] NR - not reported.

[e] Some intermittent emissions are vented without control.

[f] Petro-Tex's Houdry units have been shut down.

of the total regeneration air flow, in which most of the VOC is concentrated (during the transition from the production to the regeneration phase of the cycle), was diverted through the catalytic oxidation reactors. Operation of the oxidation reactors was cyclic. During 20% of the time cycle the oxidation reactor was heated as combustion of vented VOC occurred. For the remaining 80% of the time cycles air was passed through the reactor, cooling the bed and transmitting the stored energy to the heat recovery boiler. The installed capital cost (1975) of the catalytic oxidation reactors was approximately $750,000 for each Houdry train.

2. Arco Chemical Co. - Channelview, TX
Butadiene is currently produced by extraction from ethylene plant by-product streams, with furfural used as the extraction solvent. Until 1976 butadiene was totally produced by the catalytic dehydrogenation of butane (Houdry process). These Houdry units are no longer operating. Prior to the shutdown of the Houdry units the dehydrogenation reactor vent emissions were controlled with fixed-bed catalytic converters, which processed the entire regeneration air stream. These converters reportedly attained a VOC removal efficiency of approximately 50%, with an installed capital cost (1976) of $1,030,000 per Houdry train.

3. Firestone Synthetic Rubber and Latex Co. - Orange, TX
Butadiene is currently produced by oxidative dehydrogenation of butenes and by a modified Houdry process. Acetonitrile (ACN) and cuprous ammonium acetate solution (CAA) are used as the respective solvents in the two processes. Other variations between the Firestone butane dehydrogenation (Houdry) process and the model process are (1) Firestone operates its Houdry unit to produce both butadiene and butylenes, which reduces the butadiene yield; (2) the waste heat recovery boiler is downstream of the emission control device; (3) the boiler bottoms are transferred to a pressurized sphere. The Firestone Houdry/CAA emissions based on a 1975 emissions inventory and given in Table D-2 are significantly higher than those presented in Table IV-1.

Variations between the Firestone oxidative dehydrogenation process and the model process are (1) acetonitrile (ACN) is used as the extraction solvent; (2) the reactor temperatures are lower; (3) the butane feed is heated with steam so that no flue gas is generated; (4) absorption column ("sponge oil absorber")

Table D-2. Firestone Emissions

Source	Emissions [tons/yr (10^3 g)]	Emission Ratio (kg/Mg)[a]
Flue gas	97.8 (88,802.4)	1.78
Reactor vent		
Uncontrolled	526 (477,608)	
Controlled	5.21 (4,730.7)	0.09
Intermittent process emissions	Unknown	Unknown
Storage and handling (lower than actual)	1.94 (1,761.5)	0.04
Secondary	40.55 (36,819.4)	0.74
Fugitive (low)	14.3 (12,984.4)	0.26
Total (with Houdry incinerator) = 159.8 tons/yr, or 145,098 X 10^3 g		
Oxo/ACN/Iso Process (production from April 1979 = 53,761 tons/yr, or 48,814 X 10^6)		
Flue gas	31.9 (28,965.2)	0.59
Absorption column vent (uncontrolled)	197 (178,876)	3.66
Intermittent process emissions	Unknown	Unknown
Storage and handling (low)	0.02 (18.16)	0.0004
Secondary	10.75 (9,761)	0.20
Fugitive (low)	14.3 (12,984.4)	0.27
Total	254.0 (230,604.8)	4.72

[a] kg of emissions per Mg of product produced.

vent emissions are not controlled by catalytic or thermal oxidation, with significantly higher emission levels (estimated emissions and emission ratios for the Firestone Oxo/ACN/Iso process are given in Table A-2); (5) the Firestone reactor effluent composition is somewhat different from that in Table III-2 (see Table D-3 for comparative compositions).

4. El Paso Products Co. - Odessa, TX
Butadiene is currently produced by the dehydrogenation of butane (Houdry process). Separation and purification of butadiene are attained by a cuprous ammonium acetate solution (CAA) liquid-liquid extraction process.

The emission ratio for the purification process (fugitive emissions only) was estimated by El Paso to be 0.0425 kg per Mg of butadiene produced.

5. Exxon Chemical Co. USA - Baton Rouge, LA
Butadiene is currently produced by extraction from ethylene plant by-product streams. The Nippon Zeon Co. dimethyl formamide extractive distillation process is used. Other variations between the Exxon process and the model process are as follows: (1) the Exxon process does not use a hydrogenation reactor to convert the acetylenes to olefins; vinyl acetylene and methyl acetylene are separated and are then diluted with natural gas and C_4 hydrocarbons and burned in a steam boiler as auxiliary fuel; (2) some pressure-relief devices are vented to the atmosphere, not to a flare.

Estimated uncontrolled and controlled emission ratios are given in Table D-4.

6. Monsanto Co. - Chocolate Bayou, TX
Butadiene is currently produced by extraction from ethylene plant by-product streams. The primary variations between the Monsanto process and the model process are as follows:

   1. A methyl acetylene column is not used (C_3's are removed in the ethylene plant).
   2. The mixed C_4's fed to recovery are washed with water to remove carbonyl compounds.

Table D-3. Firestone Oxo Reactor Effluent Composition

Component	Composition (wt %) IT Enviroscience	Composition (wt %) Firestone[a,b]
Oxygen	2.86	0.04
Nitrogen	45.14	46.20
Carbon dioxide	8.57	6.80
Carbon monoxide		0.26
Methane	0.29	0.04
C_2's	0.86	0.10
C_3's	1.14	0.05
n-Butane	1.14	5.60
Isobutane	1.71	0.02
Iosbutene	3.14	nil
1-Butene	5.43	2.40
Trans-2-butene	4.86	6.20
Cis-2-butene	4.00	3.90
1,3-Butadiene	20.57	27.20
C_5's	0.29	
Neopentane		2.20
Hydrogen		0.18
	100.00	101.19

[a] Water-free basis.

[b] Actual Firestone analysis of June 3, 1979.

Table D-4. Estimates of Emission Ratios for the Exxon By-Product Butadiene Process

Source	Uncontrolled Emission Ratio[a] (kg/Mg)	Reduction (%)	Controlled Emission Ratio[a] (kg/Mg)
Vinylacetylene, methyl acetylene column vents	66.83	99	0.67
Normal process emissions (common vent)	0.99	95	0.05
Intermittent emissions	0.014	None	0.014
Storage and handling	0.01	None	0.01
Secondary	0.15	None	0.15
Fugitive	0.54	None	0.54
Total	68.53		1.43

[a] kg of emission per Mg of butadiene produced.

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Specific emission controls are as follows:

1. Regeneration off-gas is incinerated.
2. Relief-valve emissions are discharged to a flare.
3. The column vents are recycled to the ethylene plant.

B. RETROFITTING CONTROLS

As is described in Sect. III of this report, numerous variations of the processes for production of butadiene are possible. Some of these variations influence the amount and rate of the emissions. Such variations and the resulting influence on emissions should be considered before it is decided to retrofit control devices into existing plants.

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

REPORT 8

ACETIC ANHYDRIDE

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ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Acetic anhydride was selected for consideration because preliminary estimates indicated a large production volume with a resulting potential for significant emissions of volatile organic compounds (VOC). Acetic anhydride is a liquid under ambient conditions (see Appendix A for pertinent physical properties). The predominant VOC emissions from acetic anhydride production are ethylene, propane, and propadiene.[1--4] Benzene emissions occur from three of the seven operating plants.[1,5]

B. ACETIC ANHYDRIDE USAGE AND GROWTH

Table II-1 shows end uses and percentages of production for commercial acetic anhydride. It is estimated that 90% of the commercially produced anhydride is used for the production of cellulose acetate.[6,7]

The commercial acetic anhydride capacity in the United States is currently 920 Gg/yr,[3,7,8] with the 1976 commercial production being 74% of the commercial capacity.[9] The annual growth is projected to be less than 1% as the result of a declining demand for cellulose fiber relative to other synthetic fibers.[7] Therefore commercial production is expected to remain less than 80% of the current commercial capacity through 1982. The unavailability of acetic acid feedstock is the only possible factor that could restrict commercial acetic anhydride production.[8] No planned commercial capacity changes have been identified. In addition to the commercial capacity, a plant owned by the United States Army has a reported capacity of 272 Gg/yr.[10]

C. DOMESTIC PRODUCERS

There were three commercial companies and one government-owned plant producing acetic anhydride at the end of 1978. Table II-2 lists the producers, locations, capacities, and processes.[1--3,7,11,12] Figure II-1 shows the plant locations. For only about 25% of the existing commercial capacity, virgin acetic acid is used exclusively as feedstock; the remaining commercial capacity is based partly on recovered acetic acid, a reaction by-product from cellulose acetate manufacture.[7,8] The military capacity is also based on recovered acetic acid, a by-product from

Table II-1. Commercial Acetic Anhydride Usage and Growth*

End Use	Production for 1977 (%)
Cellulose acetate	90
Other acetate esters and misc.	8.6
Aspirin	1.4
Exports	Negligible

*See ref 7.

Table II-2. Acetic Anhydride Capacity[a]

Producer	Capacity for 1977 (Gg)	Process
Celanese Chemical Co., Inc.[b] Pampa, TX	136[c]	Acetic acid pyrolysis with benzene; acetic acid pyrolysis
Celanese Fibers Co. Narrows, VA	113	Acetic acid pyrolysis with benzene
Rock Hill, SC	113	Acetic acid pyrolysis with benzene
Tennessee Eastman Co. Kingsport, TN	440[d]	Acetic acid pyrolysis
Union Carbide Corp. Brownsville, TX	91[c]	Same as above
Avtex Fibers, Inc.[e] Meadville, PA	27	Same as above
Commercial total	920	
Holston Army Ammunition Plant, Holston, TN	272[f]	Same as above

[a] See ref 7.

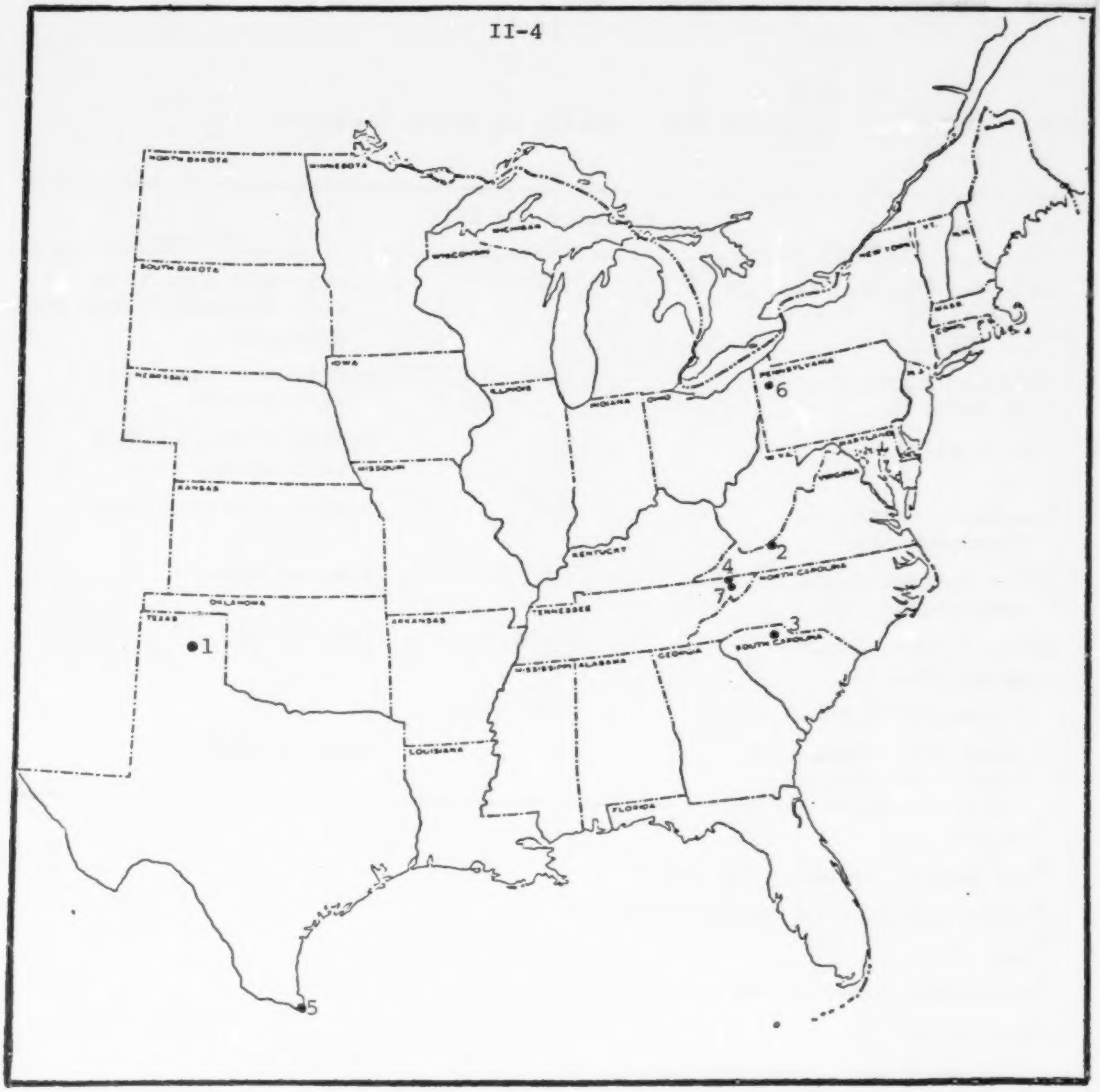
[b] Two separate plants; see ref 8.

[c] Virgin acetic acid used exclusively.

[d] See ref 3.

[e] Previously owned by FMC Corp., plant is idle; see ref 11.

[f] See ref 10.


NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
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MASS
CONN
NEBRASKA
IOWA
ILLINOIS
INDIANA
OHIO
PENNSYLVANIA
6
MARYLAND
VIRGINIA
KANSAS
MISSOURI
KENTUCKY
2
4
7
NORTH CAROLINA
OKLAHOMA
TEXAS
1
ARKANSAS
TENNESSEE
3
SOUTH CAROLINA
MISSISSIPPI
ALABAMA
GEORGIA
LOUISIANA
FLORIDA
5

(1) Celanese Chemical Co., Inc., Pampa, TX
(2) Celanese Fibers Co., Narrows, VA
(3) Celanese Fibers Co., Rock Hill, SC
(4) Tennessee Eastman Co., Kingsport, TN
(5) Union Carbide Corp., Brownsville, TX
(6) Avtex Fibers, Inc., Meadville, PA
(7) Holston Army Ammunition Plant, Holston, TN

Fig. II-1. Locations of Acetic Anhydride Plants

manufacture of explosives.[10] Apparently all existing operating capacity is based on pyrolysis of acetic acid to ketene.[1,2,11,12] There are usually no co-products resulting from this process.[6] However, a portion of the intermediate, ketene, can be diverted for direct usage in preparing diketene, which is used for a number of specialty products.[13,14]

Companies that produce acetic anhydride are listed below:

1. Celanese Corporation
   Nearly 40% of the acetic anhydride capacity is based exclusively on the use of virgin acetic acid.[8] The remaining capacity is based partly on acetic acid recovered as a by-product of cellulose acetate manufacture.[8] The resulting acetic anhydride is used as feedstock for additional cellulose acetate production.[15] A process developed by Celanese and based on pyrolysis of acetic acid to ketene, with benzene used as a quench and drying agent, is used in three of their plants.[1,5]

2. Tennessee Eastman Company
   Using a method based on a process purchased from Wacker, Tennessee Eastman produces acetic anhydride from acetic acid recovered as a by-product of cellulose acetate production and from captive acetic acid. The Kingsport plant represents a number of production trains that are tied together for materials handling and storage and waste treatment. A portion of the intermediate, ketene, is used to produce diketene.[3,12,14]

3. Union Carbide Corporation
   Acetic anhydride is produced from captive acetic acid. The plant operating at Brownsville is based on a design licensed by Tennessee Eastman Co.[2]

4. Avtex Fibers, Inc.
   It is assumed that, until the plant became idle, acetic anhydride was produced from acetic acid recovered from cellulose acetate production and from purchased acetic acid.[7,15] The plant is not expected to resume operations.[11] The process used was pyrolysis of acetic acid to ketene; diketene was produced as a co-product.[16]

5. Holston Army Ammunition Plant

At this plant, which uses Tennessee Eastman Co. technology and is operated by Tennessee Eastman Co., acetic anhydride is produced from acetic acid recovered from an explosives manufacturing process and from purchased acetic acid. The resulting acetic anhydride is used captively.[10]

D. REFERENCES*

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2. J. A. Key, IT Enviroscience, Inc., Trip Report on Visit to Union Carbide Corp. Plant at South Charleston, WV, Dec. 7, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
3. Tennessee State Air Permits for Tennessee Eastman Corp.
4. Responses by Tennessee Eastman (Aug. 15, 1972) to EPA request for information on emissions from acetic anhydride manufacture.
5. Correspondence dated January 1979 from R. H. Maurer, Celanese Chemical Co., Inc., to R. W. Helsel, IT Enviroscience, Inc. (documentation on file at IT Enviroscience, Inc., Knoxville, TN).
6. F. S. Wagner, Jr., "Acetic Anhydride," pp. 151--161 in Kirk-Othmer Encyclopedia of Chemical Technology, 3d ed., Vol. 1, edited by M. Grayson et al., Wiley-Interscience, New York, 1978.
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10. Phone conversation Sept. 7, 1978, between David Mascone, EPA, and Charles Mueller, Holston Army Ammunition Plant (documented in EPA file).
11. Personal correspondence dated May 8, 1978, from Avtex Fibers, to D. R. Goodwin, Emission Standards and Engineering, USEPA.
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15. T. Wallace, "Cellulose Acetate and Triacetate Fibers," pp. 543.3622G--M in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (November 1976).

16. Responses by FMC Corp. (Sept. 20, 1972) to EPA for the Petrochemical Emissions Survey Questionnaire.

*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

Three different continuous processes for manufacturing acetic anhydride, each one starting with a different feedstock, are described in recent literature.[1--3] In one, the acetaldehyde-oxidation process, acetic anhydride is produced as a co-product of acetic acid.[3] It is assumed that this process is no longer being used domestically but it may still be in use outside the United States.[4] Another process involves the pyrolysis of acetone.[3] The third method, which is apparently being used today for nearly all domestic acetic anhydride production, is by pyrolysis of acetic acid.[5--8] In this process, acetic acid is pyrolyzed to ketene, which is reacted with additional acetic acid to produce the anhydride. Two process configurations are employed, differing in the manner in which the ketene/acetic acid reaction is carried out. In the predominant process configuration, developed originally by Wacker, ketene gas is separated from the condensables by cooling and phase separation and is then contacted with acetic acid in absorbers.[3,5] This configuration has been selected for the model plant*, since it is representative of the majority of production. In the other process configuration, developed by Celanese, the pyrolysis reactor effluent gas is quenched with benzene,[6,9] as is discussed in "Process Variation."

Most commercial acetic anhydride is produced in conjunction with acetic acid production at the same site.[10] Also, most commercial acetic anhydride production is consumed at the same site for the manufacture of cellulose acetate.[11] A portion of the ketene produced in the pyrolysis of acetic acid can be diverted and used to produce other products.[12] Since ketene is a very reactive gas, it is converted immediately to the intended product rather than being stored or shipped.[12]

B. MODEL PROCESS FOR MANUFACTURE OF ACETIC ANHYDRIDE

Acetic anhydride is produced by the following chemical reactions:

Pyrolysis of acetic acid to ketene

$$\underset{\text{(acetic acid)}}{CH_3COOH} \longrightarrow \underset{\text{(ketene)}}{CH_2{=}C{=}O} + \underset{\text{(water)}}{H_2O}$$

---

*See p I-2 for discussion of model plants.

Addition of ketene and acetic acid to produce acetic anhydride

$$\underset{\text{(acetic acid)}}{CH_3COOH} \quad + \quad \underset{\text{(ketene)}}{CH_2{=}C{=}O} \quad \longrightarrow \quad \underset{\text{(acetic anhydride)}}{(CH_3CO)_2O}$$

The model process for the manufacture of acetic anhydride from acetic acid is shown in Fig. III-1. This continuous process has been described in detail in the literature,[3] although there may be some variations in the flow patterns of the ketene absorber and gas scrubber systems and the distillation trains.[5,7]

The first step in the model process is pyrolysis. Acetic acid (Stream 1) is vaporized and fed under vacuum to the pyrolysis furnace. A catalyst, normally triethylphosphate, is added to the feed stream. Typically a number of pyrolysis reactors are operated in parallel for each production unit. The reactors are operated at about 700°C and 13,000 to 26,000 Pa at the outlet. The yield of ketene is influenced by pressure, temperature, catalyst, and reaction time. Lower yields result in higher amounts of by-products such as methane, ethylene, and carbon monoxide. Ammonia can be added to the reactor effluent to neutralize the catalyst and stabilize the ketene. The effluent (Stream 2) is cooled before it enters a phase separator, where water of reaction and most of the unconverted acetic acid are separated as a condensate from the ketene and reaction by-product gas. The weak acetic acid condensate (Stream 3) is combined with dilute acetic acid effluent from the scrubbers and acetic acid column overhead and sent to a light-ends column.[3,5,7] It is assumed that ammonium metaphosphate formed from neutralization of the catalyst is contained in Stream 3 and ultimately is discharged from the process in the dilute acetic acid (Stream 15).

Acetic anhydride is produced in the second process step. In this step the gaseous ketene stream (Stream 4) from the phase separator is contacted with glacial acetic acid liquid (Stream 5) in two absorption columns operated in series under reduced pressure (6,600 to 20,000 Pa) and near-ambient temperature (30 to 40°C). It has been reported that liquid-ring rotary compressors can be used in place of absorption columns and vacuum jets for the ketene--acetic acid reaction.[4] The crude acetic anhydride liquid (Stream 6) exiting the absorption columns is collected and sent to product purification.[3]

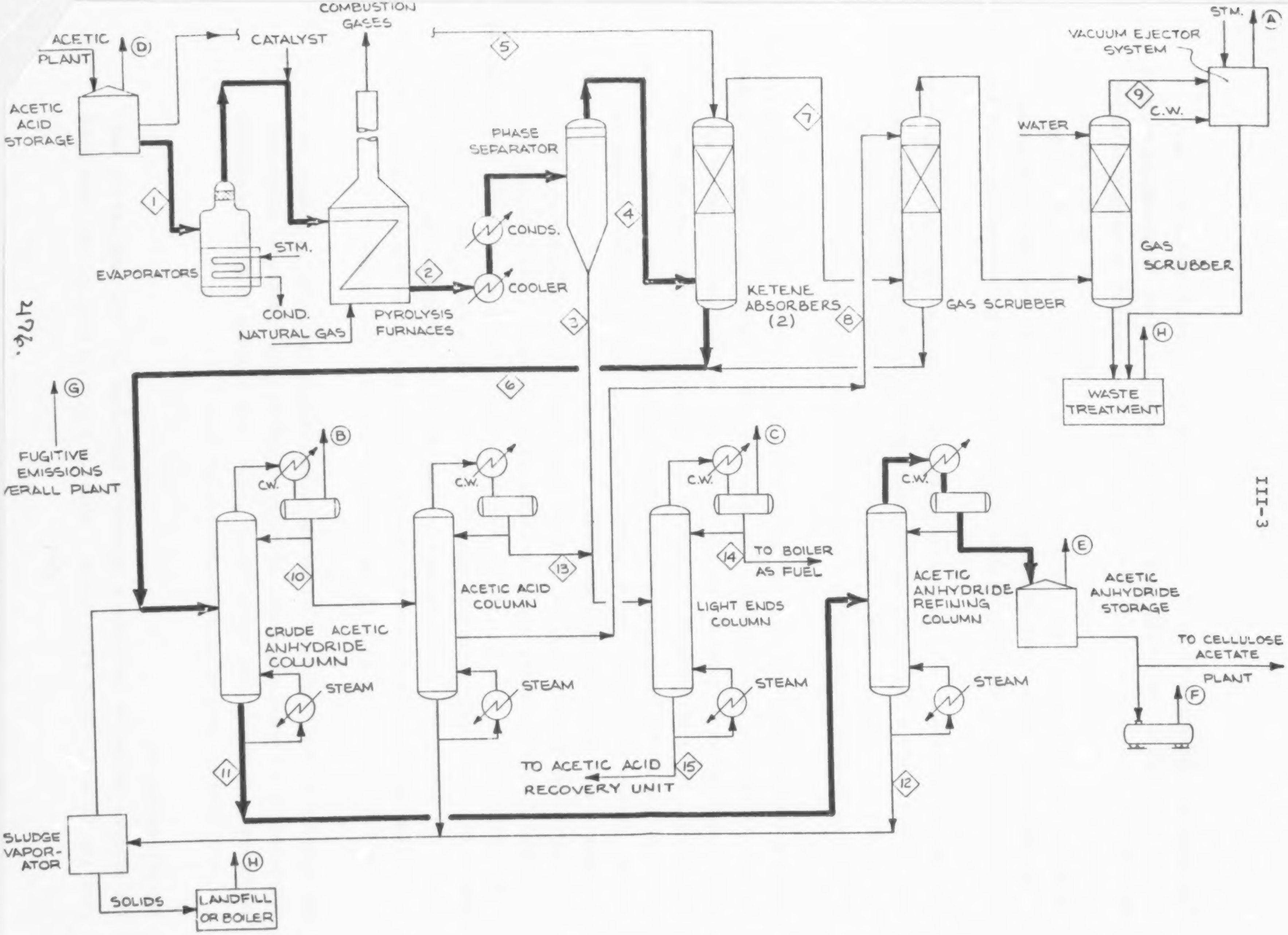
ACETIC PLANT
(D)
CATALYST
COMBUSTION GASES
5
STM.
(A)
VACUUM EJECTOR SYSTEM
ACETIC ACID STORAGE
1
EVAPORATORS
STM.
COND.
NATURAL GAS
PYROLYSIS FURNACES
2
CONDS.
COOLER
PHASE SEPARATOR
4
3
KETENE ABSORBERS (2)
7
8
GAS SCRUBBER
WATER
9
C.W.
GAS SCRUBBER
WASTE TREATMENT
(H)
6
(G)
FUGITIVE EMISSIONS
/ERALL PLANT
C.W.
(B)
10
CRUDE ACETIC ANHYDRIDE COLUMN
STEAM
11
C.W.
13
ACETIC ACID COLUMN
STEAM
C.W.
(C)
14
TO BOILER AS FUEL
LIGHT ENDS COLUMN
STEAM
15
TO ACETIC ACID RECOVERY UNIT
C.W.
ACETIC ANHYDRIDE REFINING COLUMN
STEAM
12
(E)
ACETIC ANHYDRIDE STORAGE
TO CELLULOSE ACETATE PLANT
(F)
SLUDGE VAPOR-ATOR
SOLIDS
LANDFILL OR BOILER
(H)

Fig. III-1. Flow Diagram for Uncontrolled Acetic Anhydride Model Process

The absorber off-gas (Stream 7), which contains the reaction by-product gas, acetic acid, acetic anhydride, and traces of ketene, is sent to scrubbing columns for removal of acetic acid and acetic anhydride. The primary scrubbing solution (Stream 8), a strong acetic acid, results from the distillation of the acetic acid fraction (Stream 10) that is separated from the acetic anhydride in the crude anhydride column. The final scrubber uses water as a scrubbing solution, with the spent solution normally discharged to the sewer for wastewater treatment.[3,5,7]

The off-gas (Stream 9) from the scrubber system, containing the reaction by-product gas, passes through the vacuum system, which provides the required reduced pressures throughout the reaction and absorption systems.[3,5,7] Vacuum jet ejectors are assumed to be used as the vacuum source for the model process.

Crude acetic anhydride (Stream 6), which contains about 10% acetic acid, is purified by two atmospheric distillations. In the crude acetic anhydride column the acetic acid is removed as an overhead stream (Stream 10) for further processing and recycling. The acetic anhydride (Stream 11) is then distilled overhead in the acetic anhydride refining column, with heavy impurities being removed as a bottoms stream (Stream 12). Acetic acid removed from the acetic anhydride (Stream 10) is concentrated in a distillation column; the strong acetic acid fraction is recycled to the scrubber system, and the weak acetic acid overhead (Stream 13) is combined with the phase separator condensate (Stream 3) and distilled in the light ends column. This separation removes traces of reaction by-products (Stream 14) before the weak acetic acid solution (Stream 15) is sent to an acetic acid recovery unit. The acetic acid recovery unit is considered to be part of the acetic acid production plant or the cellulose acetate production plant at the same site. This unit is not included as part of the acetic anhydride model process.[3,5,7]

The bottoms stream (Stream 12) from the acetic anhydride refining column is processed in a sludge evaporator to recover acetic acid and acetic anhydride, which are recycled to the distillation train. The residue from the evaporator is landfilled or used as supplemental boiler fuel.[5--7]

C. PROCESS VARIATION

The process variation involves a different technique for the combination and reaction of acetic acid with ketene. This is a proprietary process developed by Celanese and is used in three of its plants.[13] A simplified sketch is shown in Fig. III-2. In the process variation the pyrolysis reactor discharge (Stream 2), containing ketene, water, acetic acid, and by-products, is quenched with liquid benzene (Stream 3). The benzene and water are removed from the resulting mixture and processed for recovery of benzene for recycling. The water fraction (Stream 4) is processed as part of waste handling. The water (Stream 5) is discharged to a wastewater treatment plant. The dehydrated ketene and acetic acid react to form acetic anhydride (Stream 6), which is distilled to separate unreacted acetic acid (Stream 7) and to remove impurities (Stream 8). The weak acetic acid (Stream 7) is sent to an acetic acid recovery unit as with the model process. The impurities (Stream 8) are processed as part of waste handling.[6,9]

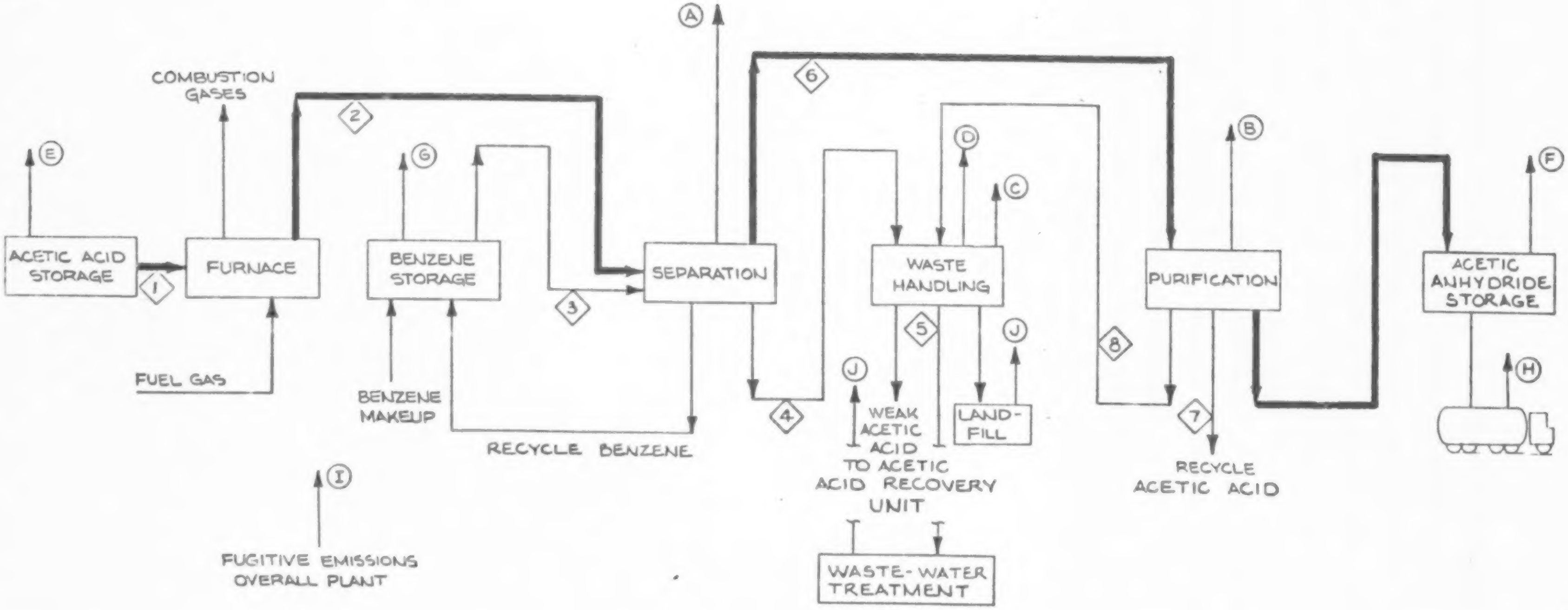
ACETIC ACID STORAGE
E
1
FURNACE
COMBUSTION GASES
FUEL GAS
2
BENZENE STORAGE
G
BENZENE MAKEUP
3
RECYCLE BENZENE
I
FUGITIVE EMISSIONS OVERALL PLANT
SEPARATION
A
6
4
J
WEAK ACETIC ACID TO ACETIC ACID RECOVERY UNIT
WASTE HANDLING
D
C
5
J
LAND-FILL
WASTE-WATER TREATMENT
8
PURIFICATION
B
7
RECYCLE ACETIC ACID
ACETIC ANHYDRIDE STORAGE
F
H

Fig. III-2. Simplified Sketch for
Uncontrolled Acetic Anhydride Process Variation Using Benzene Quench (See Ref. 6)

D. REFERENCES*

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13. Correspondence January 1979 from R. H. Maurer, Celanese Chemical Co., Inc., to R. W. Helsel, IT Enviroscience, Inc. (documentation on file at IT Enviroscience, Inc., Knoxville, TN).

*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. TYPICAL PLANT

The capacity of the typical plant* developed for this study is 110 Gg/yr, based on 8760 hr of operation per year.** Although not an actual operating plant, the size of the plant is typical of most operating production units or trains. The plant utilizes the model process described in Sect. III. It is representative of today's acetic anhydride manufacturing industry, which utilizes current engineering technology. For the following description of emissions a plant using the process variation is defined as having the same capacity as the typical plant.

B. SOURCES AND EMISSIONS

Uncontrolled emission rates of CO and VOC from the process for the typical plant are summarized in Table IV-1 and are discussed below. Uncontrolled emission rates of VOC and benzene from the process for a plant using the process variation are summarized in Table IV-2 and are discussed below.

1. Reactor By-Product Gas

The largest process emission of VOC is from the vacuum jet system (Source A, Fig. III-1), which discharges the reactor by-product gas components not removed in the ketene absorbers or gas scrubber system. This emission contains methane,

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*See p I-2 for a discussion of typical or model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

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Table IV-1. Uncontrolled Emissions of CO and VOC from Typical Acetic Anhydride Plant Using Model Process

		Emissions			
	Stream Designation	Ratio (g/kg)[a]		Rate (kg/hr)	
Source	(Fig. III-1)	CO	VOC	CO	VOC
Reactor by-product gas	A	7.00	4.50	88.2	56.5
Column vents	B,C		0.700		8.82

[a] g of emission per kg of acetic anhydride produced.

Table IV-2. Uncontrolled Emissions of Total VOC and Benzene from Acetic Anhydride Plant Using Process Variation

		Emissions			
	Stream Designation	Ratio (g/kg)[a]		Rate (kg/hr)	
Source	(Fig. III-2)	Total VOC	Benzene	Total VOC	Benzene
Reactor by-product gas	A	31.0	4.6	389	57.8
Column vents	B,C,D	2.13	0.217	26.8	2.73

[a] g of emission per kg of acetic anhydride.

CO, and CO_2, in addition to various VOC, that result from by-product reactions during the acetic acid pyrolysis. Table IV-3 shows the typical composition of the off-gas based on both measured and estimated composition data from several sources.[1--5] Based on these composition data approximately 3% of the acetic acid feed to pyrolysis is converted to by-product gas. The emission quantity and composition are related to the degree of by-product reactions, the production rate, and the impurities, such as formic or propionic acid, that may be contained in the acetic acid feed. At capacity operation the uncontrolled VOC emission is estimated to be 56.5 kg/hr.

For the plant using the process variation the VOC emission ratio was calculated based on emission data from the plant visited and the assumption that its capacity was one half the total capacity indicated in Table II-2 for that producing location. At capacity operation the uncontrolled VOC emission (Source A, Fig. III-2) is estimated to be 188 kg/hr for this plant. Benzene would be present in the by-product gas, in addition to methane, CO, CO_2, and other VOC indicated in Table IV-3. The by-product gas represents the largest source of benzene emission. The amount of benzene will be primarily related to the amount of total by-product gas. Based on capacity operation the uncontrolled benzene emission rate is estimated to be 29.1 kg/hr.

2. Column Vents

These vents emit the dissolved gases and uncondensed VOC from the crude anhydride (Source B, Fig. III-1) and light-ends (Source C, Fig. III-1) distillation columns in quantities related to production. The total uncontrolled VOC emission rate is estimated to be 8.82 kg/hr for the typical plant operating at capacity.

For the plant using the process variation it is assumed that there are three different column vents (Sources B, C, and D, Fig. III-2). The uncontrolled emission rates estimated for total VOC and benzene are shown in Table IV-2.

3. Storage and Handling Emissions

Emissions result from the storage and handling of acetic acid, acetic anhydride, and in-process streams. Sources of losses are shown in Fig. III-1 (Sources D, E and F). Storage and handling emissions from the entire synthetic organic chemicals industry are discussed in a separate report.[6]

Table IV-3. Composition of Reactor By-Product Gas in Typical Acetic Anhydride Plant[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
VOC		
Propane	4	0.73
Ethylene	8	1.5
Propadiene	10	1.9
Other VOC[c]	2	0.37
Total VOC	24	4.50
Other components		
Methane	5	0.95
Carbon monoxide	37	7.0
Carbon dioxide	27	5.0
Others[d]	7	1.3
Total	100	18.75

[a] See refs. 1--5.

[b] g of emission per kg of acetic anhydride.

[c] Includes hydrocarbons such as propylene, butylene, and butadiene.

[d] Includes nitrogen, oxygen, and water.

4. Fugitive Emissions

Process pumps and valves are potential sources of fugitive emissions (Source G). Fugitive emissions are discussed in a separate report.[7]

5. Secondary Emissions

Secondary VOC emissions can result from the handling and disposal of process-waste liquid streams and solid residues. Two potential sources (H) are indicated in Fig. III-1 for the typical plant. Evaluation of the potential emissions from disposal of these and other wastes from the entire SOCMI are covered by a separate EPA report.[8]

Secondary benzene emissions (Source I, Fig. III-2) can result similarly from a plant using the process variation.

C. OTHER PROCESSES

No data are available on emissions from domestic processes used previously for production of acetic anhydride or for those used outside the United States today.

D. REFERENCES*

1. R. W. Helsel, IT Enviroscience, Inc., Trip Report on Visit to Celanese Chemical Corp. Plant at Pampa, TX, Aug. 23, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. J. A. Key, IT Enviroscience, Inc., Trip Report on Vist to Union Carbide Corp., Plant at South Charleston, WV, Dec. 7, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

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V. APPLICABLE CONTROL SYSTEMS

A. REACTOR BY-PRODUCT GAS

The gas that exits the vacuum system vent can be thermally oxidized for effective control of the VOC. The amount of CO, methane, ethylene, and other hydrocarbons present in this gas provides more than adequate fuel value. Apparently, all operating commercial plants, including those using the model process and those using the process variation, are practicing thermal oxidation.[1–4]

A reduction of 99% in VOC and CO emissions was used for the calculation of the controlled emissions given in Table V-1. Analysis of the pyrolysis furnace stack at one plant indicates that greater than 99% removal can be achieved.[1] During startup or process upsets the reactor by-product gas may be discharged as an uncontrolled emission. Startup would be expected to occur four to six times a year for each furnace.[1] Startup emission quantities were not calculated and are not considered in the 99% reduction assumption.

For plants using the process variation, thermal oxidation of the reactor by-product gas will be effective for controlling benzene emissions. Table V-2 gives the data on controlled benzene emissions. A removal efficiency of 99% was assumed, based on interpretation of vent gas and flue gas analysis from one plant.[1]

B. COLUMN VENTS

The emissions from the column vents can be controlled by piping them to the pyrolysis furnace (with the reactor by-product gas) as discussed in Sect. V.A. The cost effectiveness of this control was not evaluated.

Analysis of column vent emissions from a plant using the process variation indicates that the fuel content is very low and that the moisture content is relatively high.[1] A vent condenser would effectively reduce the water content, which represented more than half the emission quantity, if this was necessary to ensure proper thermal oxidation in the pyrolysis furnace. For the plant visited that uses the process variation, column vents that emit benzene are controlled by thermal oxidation in the pyrolysis furnace.[4] A reduction of 99% was used in the calculation of the controlled total VOC and benzene emissions given in Tables V-1 and V-2.

Table V-1. VOC and CO Emissions from Controlled Sources in Typical Acetic Anhydride Plant

Source	Stream Designation (Fig.III-1)	Control Device or Technique	Emission Reduction (%)	Emissions			
				Ratio (g/kg)*		Rate (kg/hr)	
				CO	VOC	CO	VOC
Reactor by-product gas	A	Thermal oxidizer (pyrolysis furnace)	99	0.070	0.045	0.882	0.565
Column vents	B,C	Thermal oxidizer (pyrolysis furnace)	99		0.007		0.088

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[*] g of emission per kg of acetic anhydride.

Table V-2. Total VOC and Benzene Emissions from Controlled Sources in a Plant Using the Process Variation

Source	Stream Designation (Fig.III-2)	Control Device or Technique	Emissions Reduction (%)	Emissions Ratio* (g/kg)* Total VOC	 Benzene	 Rate (kg/hr) Total VOC	 Benzene
Reactor by-product gas	A	Thermal oxidizer (pyrolysis furnace)	99	0.31	0.046	3.89	0.578
Column vents	B,C,D	Thermal oxidizer (pyrolysis furnace)	99	0.021	0.002	0.268	0.027

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[*] g of emission per kg of acetic anhydride.

C. STORAGE AND HANDLING SOURCES

Controls for storage and handling emissions from the entire synthetic organic chemicals manufacturing industry are discussed in a separate EPA report.[5]

D. FUGITIVE-EMISSION SOURCES

Controls for fugitive emissions from the synthetic organic chemicals manufacturing industry are discussed in a separate EPA report.[6]

F. REFERENCES*

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2. R. W. Helsel, IT Enviroscience, Inc., Trip Report on Visit to Tennessee Eastman Co. Plant at Kingsport, TN, Jan. 24, 1978 (on file at EPA, ESED, Research Triangle Park, NC).
3. J. A. Key, IT Enviroscience, Inc., Trip Report on Visit to Union Carbide Corp. Plant at South Charleston, WV, Dec. 7, 1977 (on file at EPA, ESED, Research Triangle Park, NC).
4. Correspondence dated Jan. 30, 1979, from R. H. Maurer, Celanese Chemical Co., Inc., to R. W. Helsel, IT Enviroscience, Inc. (documentation on file at IT Enviroscience, Inc., Knoxville, TN).
5. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).
6. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

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*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. CONTROL COST IMPACT

Costs and cost-effectiveness data for control of VOC emissions and benzene emissions resulting from production of acetic anhydride were not developed. All operating commercial plants are presently utilizing thermal oxidation for the reactor by-product gas, and it is estimated that additional capital costs for including the column vents would be low in most cases, depending on piping costs. Based on industry response regarding the equipment requirements for accomplishing thermal oxidation of the reactor by-product gas, capital costs would be considered to be low for new sources.[1,2] It is assumed that labor costs, maintenance costs, and capital charges would be low and that the recovery credits for fuel value present in the reactor by-product gas would result in a net operating margin for utilization of thermal oxidation for the reactor by-product gas and column vents.

1. Typical Plant

The environmental impact of the application of the described control systems to the typical new plant would be a CO emission reduction of 764.9 Mg/yr and a VOC emission reduction of 566.2 Mg/yr, as shown in Table VI-1. The environmental impact from the described control systems for the plant using the process variation would be a total VOC reduction of 1862 Mg/yr, including a benzene reduction of 274.6 Mg/yr, as shown in Table VI-2.

2. Industry

Emission sources, control levels, and emission ratios for the industry are summarized in Table VI-3. From emission data reported by producing commercial acetic anhydride plants[1-4] the emission ratios for the industry have been estimated and are also shown in Table VI-3. Secondary emissions are not considered. These values are based on 70% of the production manufactured by processes comparable to the model process and 30% manufactured by processes comparable to the process variation. These values show that the industry processes are about 86% controlled for VOC. Based on the reactor off-gas being considered as the only CO emission the industry processes are 99% controlled for CO. Industry processes comparable to the process variation are about 96% controlled for benzene. With an estimated 1978 production level of 694 Gg the process emissions from industry are estimated to be 48.6 Mg of CO, 719 Mg of VOC, and 9.4 Mg of benzene.

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Table VI-1. Environmental Impact of Controlled Sources in a Typical Acetic Anhydride Plant*

Source	Stream Designation (Fig.III-1)	Control Device or Technique	Emission Reduction			
			CO		Total VOC	
			(%)	(Mg/yr)	(%)	(Mg/yr)
Reactor by-product gas	A	Thermal oxidizer (pyrolysis furnace)	99	764.9	99	490.0
Column vents	B,C	Thermal oxidizer (pyrolysis furnace)		———	99	76.2
Total				764.9		566.2

*Storage and handling fugitives and secondary emissions not included.

Table VI-2. Environmental Impact of Controlled Sources in Acetic Anhydride Plant Using the Process Variation*

Source	Stream Designation (Fig.III-2)	Control Device or Technique	Emission Reduction			
			Total VOC		Benzene	
			(%)	(Mg/yr)	(%)	(Mg/yr)
Reactor by-product gas	A	Thermal oxidizer (pyrolysis furnace)	99	3380	99	501
Column vents	B,C,D	Thermal oxidizer (pyrolysis furnace)	99	232	99	23.6
Total				3612		524.6

*Storage and handling fugitive and secondary emissions not included.

Table VI-3. Emission Ratios for Industry[a]

Emission Source	Emission Ratio (g/kg)[b]		
	CO	VOC	Benzene[c]
Reactor by-product gas	0.070	0.124	0.046
Column vents	———	0.96	0.022
Total[d]	0.070	1.084	0.068

[a] "Industry" is based on 70% of active commerical plants using processes comparable to the model process and 30% using processes comparable to the process variation. Secondary emissions are not included.

[b] g of emission per kg of acetic anhydride; determined froms refs 1—3.

[c] Benzene emission ratio is based only on the plants using the process variation.

[d] Excluding storage and handling, fugitive, and secondary emissions.

B. REFERENCES*

1. R. W. Helsel, IT Enviroscience, Inc., Trip Report on Visit to Celanese Chemical Co., Inc., Plant at Pampa, TX, Mar. 1, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. R. W. Helsel, IT Enviroscience, Inc., Trip Report on Visit to Tennessee Eastman Co. Plant at Kingsport, TN, Jan. 24, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. J. A. Key, IT Enviroscience, Inc., Trip Report on Visit to Union Carbide Corp. Plant at South Charleston, WV, Dec. 7, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

4. Correspondence Jan. 30, 1979 from R. H. Maurer, Celanese Chemical Co., Inc., to R. W. Helsel, IT Enviroscience, Inc. (documentation on file at IT Enviroscience, Inc., Knoxville, TN).

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APPENDIX A

Table A-1. Physical Properties of Acetic Anhydride*

Synonyms	Acetyl oxide, acetic oxide, ethanoic anhydride
Molecular formula	$C_4H_6O_3$
Molecular weight	102.09
Vapor pressure	5.09 mm at 25°C
Melting point	-73.1°C
Boiling point	139.55°C at 1 atm
Density	1.082 g/ml at 20°C/4°C
Physical state	Liquid
Vapor density	3.50
Water solubility	Very soluble

*From: J. Dorigan *et al.*, "Acetic Anhydride," p. AI-18 in Appendix I, Rev. 1, *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals D--E)*, MTR-7248, MITRE Corp. (September 1976).

Table A-2. Physical Properties of Benzene[a]

Synonyms	Benzol, phenylhydride, coal naphtha
Molecular formula	C_6H_6
Molecular weight	78.11
Physical state	Liquid
Vapor pressure	95.9 mm at 25°C
Vapor density	2.77
Boiling point	80.1°C at 760 mm
Melting point	5.5°C
Density	0.8787 at 20°C/4°C
Water solubility	Slight (1.79 g/liter)

[a] J. Dorigan, B. Fuller, and R. Duffy, "Benzene," p AI-102 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals a-c)*, MTR-7248, Rev 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

APPENDIX B

EXISTING PLANT CONSIDERATIONS

Table B-1[1—4] lists emission controls reported to be in use by industry. To gather information for the preparation of this report three visits were made to manufacturers of acetic anhydride. Trip reports have been cleared by the companies concerned and are on file at EPA/ESED in Durham, NC.[1,2,4] Some of the pertinent information concerning process emissions from these existing acetic anhydride plants is presented in this appendix. Also included is information received with comments on the draft report Acetic Anhydride.[5,6]

A. CONTROLS AT EXISTING PLANTS

1. Tennessee Eastman Company, Kingsport, TN

The acetic anhydride plant was initially built in 1934 by a design purchased from Wacker. Many modifications and additions have been made to the original plant, the most recent one being completed in 1977. The reactor by-product gas exits the process from the vacuum jets and is collected and normally burned as supplemental fuel in the pyrolysis furnaces. This control method is considered by Tennessee Eastman to be essentially 100% effective in removing organics except during periods of startup or maintenance, when the off-gas cannot be sent to the furnace.[1]

2. Celanese Fibers Company, Narrows, VA, and Rock Hill, SC

Both plants use the acetic acid pyrolysis process with benzene quench; in addition, the Rock Hill plant has one operating unit using a proprietary Celanese process. Reportedly at one plant the total VOC in the reactor by-product gas is 31 g/kg of acetic anhydride produced and the benzene is 3.7 g/kg of acetic anhydride produced.[5]

3. Celanese Chemical Company, Pampa, TX

The acetic anhydride plant in which benzene is used as a drying agent was built in 1952 by a Celanese design. Gases formed in the pyrolysis reaction are separated from the crude acetic anhydride and compressed, the condensibles are removed by phase separation, and the noncondensibles ("decomp gas") are sent to the pyrolysis furnaces as supplementary fuel. A typical analysis by Celanese for the "decomp gas" (before and after control) is found in Table B-2.

Table B-1. Emission Control Devices Currently Used by Some Domestic Commercial Acetic Anhydride Producers

	Control Devices Used By		
Source	Tennessee Eastman Co.[a] Kingsport, TN	Celanese Chemical Co., Inc.[b] Pampa, TX	Union Carbide Corp.[c] Brownsville, TX
Reactor by-product gas	Thermal oxidizer[d]	Thermal oxidizer[d]	Thermal oxidizer[e]
Column vents	To atmosphere	To atmosphere (nonbenzene) Thermal oxidizer (benzene)	To atmosphere[f]
Storage and handling (in-process vessels)[g]	Not applicable	Thermal oxidizer	Not applicable

[a] See ref 1.

[b] See refs 2 and 3.

[c] See ref 4.

[d] Oxidized in pyrolysis furnace as supplemental fuel.

[e] Oxidized after pyrolysis furnace prior to waste heat recovery boiler.

[f] Pressure-vacuum relief valves are used.

[g] For benzene-containing streams only.

Table B-2. "Decomp Gas" Emission Data

Compound	"Decomp Gas" Feed to Furnace (wt %)	(lb/hr)	Furnace Stack (ppm)	(lb/hr)	(tons/yr)
Methane	2.2	19.51	6.9	0.053	0.23
VOC*	29.7	265.76	1.1	0.007	0.03
CO	35.2	315.3	1.6	0.021	0.09
CO_2	26.0	233.3			
Benzene	4.4	39.25			
SO_2			0.0		
NO_x			91.5	2.009	8.8
Others	6.9	61.53			
Particulates			(EPA factor)		0.8

*Volatile organic compounds other than methane.

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The other two process emission points are the steam jet ejector vents from the dirty-product still and the anhydride finishing still, which are discharged to the atmosphere. Typical vent analysis by Celanese for the combined emission from the anhydride finishing column overhead jet and the DP still overhead is as follows:

Flow (lb/hr) 560

Composition, wt %

Acetic Acid	2.9
Benzene	0.1
Acetone	1.7
Acetic Anhydride	0.3
CO_2	7.8
Water	59.9
N_2	0.5
NO_2	0.1
Air	26.4

4. Union Carbide Corporation, Brownsville, TX[4]

Acetic anhydride is produced from acetic acid by a ketene process licensed from Tennessee Eastman. The Brownsville plant was originally built in 1950 by Carthage Hydrocal Co. to produce gasoline and other fuels and chemicals from natural gas but was shut down in 1953. Standard Oil and Gas Co. acquired the plant and made additions and modifications to it; however, because of poor economics, it was shut down in 1957. Union Carbide purchased the facilities and converted the equipment to produce acetic acid, acetic anhydride, etc., in 1961. The plant was expanded in 1965.

The emissions from the vacuum ejector system on the gas scrubbers in the acetic anhydride process are controlled by burning in the process off-gas burners. The operating conditions of the Wacker off-gas burner are as follows:

Off gas flow, scfh/pph	5460/500
Off gas pressure, "H_2O	25
Off gas temperature, °C	49
Off gas specific gravity, with reference to air at 14.7 psia and 70°F	1.22
Off gas composition, mole or vol %	*
Allene and/or methyl acetylene	10.1
Butadiene	0.9
Carbon dioxide	22.8
Carbon monoxide	46.6
Ethane	0.4
Ethylene	8.7
Methane	8.5
Oxygen	0.5
Propylene	0.6
Water	0.9

*Off gas composition from analysis of sample taken on October 1, 1975; represented by the unit to be a typical composition.

B. RETROFITTING CONTROLS

As discussed in Sect. V-A, apparently all operating commercial acetic anhydride plants use thermal oxidation to control the VOC emissions in the reactor by-product gas vented from the vacuum system. Also, several plants send the column vent gases to the pyrolysis furnaces. The primary difficulty with retrofitting this control technique to the plants that are not controlled may be that the back pressure on the columns and on the vacuum systems will cause upsets in the operation of the process or will overpressure and damage the equipment. Because of the costs associated with preventing this difficulty it may be appreciably more expensive to retrofit this emission control system in existing plants than to install a control system during construction of a new plant.

F. REFERENCES*

1. R. W. Helsel, IT Enviroscience, Inc., Trip Report on Visit to Tennessee Eastman Co. at Jan. 24, 1978 (data on file at EPA, ESED, Research Triangle Park, NC).

2. R. W. Helsel, IT Enviroscience, Inc., Trip Report on Visit to Celanese Chemical Co., Inc. Pampa, TX, Mar. 1, 1978 (data on file at EPA, ESED, Research Triangle Park, NC).

3. Correspondence January 1979 from R. H. Maurer, Celanese Chemical Corp., to R. W. Helsel, IT Enviroscience, Inc. (documentation on file at IT Enviroscience, Inc., Knoxville, TN).

4. J. A. Key, IT Enviroscience, Inc., Trip Report on Visit to Union Carbide Corp. Plant at South Charleston, WV, Dec. 7, 1977 (data on file at EPA, ESED, Research Triangle Park, NC).

5. J. C. Pullen, Celanese Fibers Company, letter dated Oct. 12, 1979, to J. R. Framer, EOA, with comments on draft report Acetic Anhydride (on file at EPA, ESED, Research Triangle Park, NC).

6. R. H. Maurer, Celanese Chemical Company, Inc., letter dated Nov. 27, 1979, to J. R. Farmer, EPA, with comments on draft Acetic Anhydride Report (on file at EPA, ESED, Research Triangle Park, NC).

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REPORT 9

ACETIC ACID, FORMIC ACID, ETHYL ACETATE, METHYL ETHYL KETONE

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Prepared for
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ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

October 1980

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Acetic acid was selected for consideration because preliminary information indicated that its production causes significant emissions of volatile organic compounds (VOC), estimated as 1.5% of the total emissions from the synthetic organic chemicals industry. Formic acid, ethyl acetate, and methyl ethyl ketone (MEK) are included in the study because they are by-products from the butane oxidation process for producing acetic acid (see Fig II-1), currently the process used in manufacturing 28% of the acetic acid produced in the United States and that results in the highest ratio of total VOC emitted per kg of acetic acid produced.

Acetic acid, formic acid, ethyl acetate, and MEK are liquids under ambient conditions but are sufficiently volatile for gaseous emissions to occur during production (see Appendix A for pertinent properties). The emissions from their production consist of butane, acetaldehyde, methanol, acetic acid, ethane, methyl acetate, ethyl acetate, formic acid, MEK, ethanol, and butanol.

B. USAGE AND GROWTH

Table II-1 shows the end uses of acetic acid. The largest use is in the production of vinyl acetate monomer, which is expected to continue to grow, as is the production of purified terephthalic acid (PTA) and dimethyl terephthalate (DMT). Another large end use for acetic acid results from the production of cellulose acetate, whose precursor is acetic anhydride, which is made from acetic acid. However, little, if any, growth is expected for cellulose acetate. Future growth of acetic acid production is predicted to be 5% per year.[1]

Formic acid is used in textile dyeing and finishing, chemical synthesis, pharmaceutical synthesis, and tanning and leather treatment. Its usage is expected to grow about 4% per year. The textiles industry will continue to be the largest market for formic acid, even though it will, to some extent, be replaced by acetic acid.[2]

Ethyl acetate is used primarily as a solvent, with only 3% used in chemical synthesis. As the use of some solvents is restricted by new environmental regulations, ethyl acetate production may increase slightly despite its loss to ketones for some uses. Future growth is expected to be about 3% per year.[3]

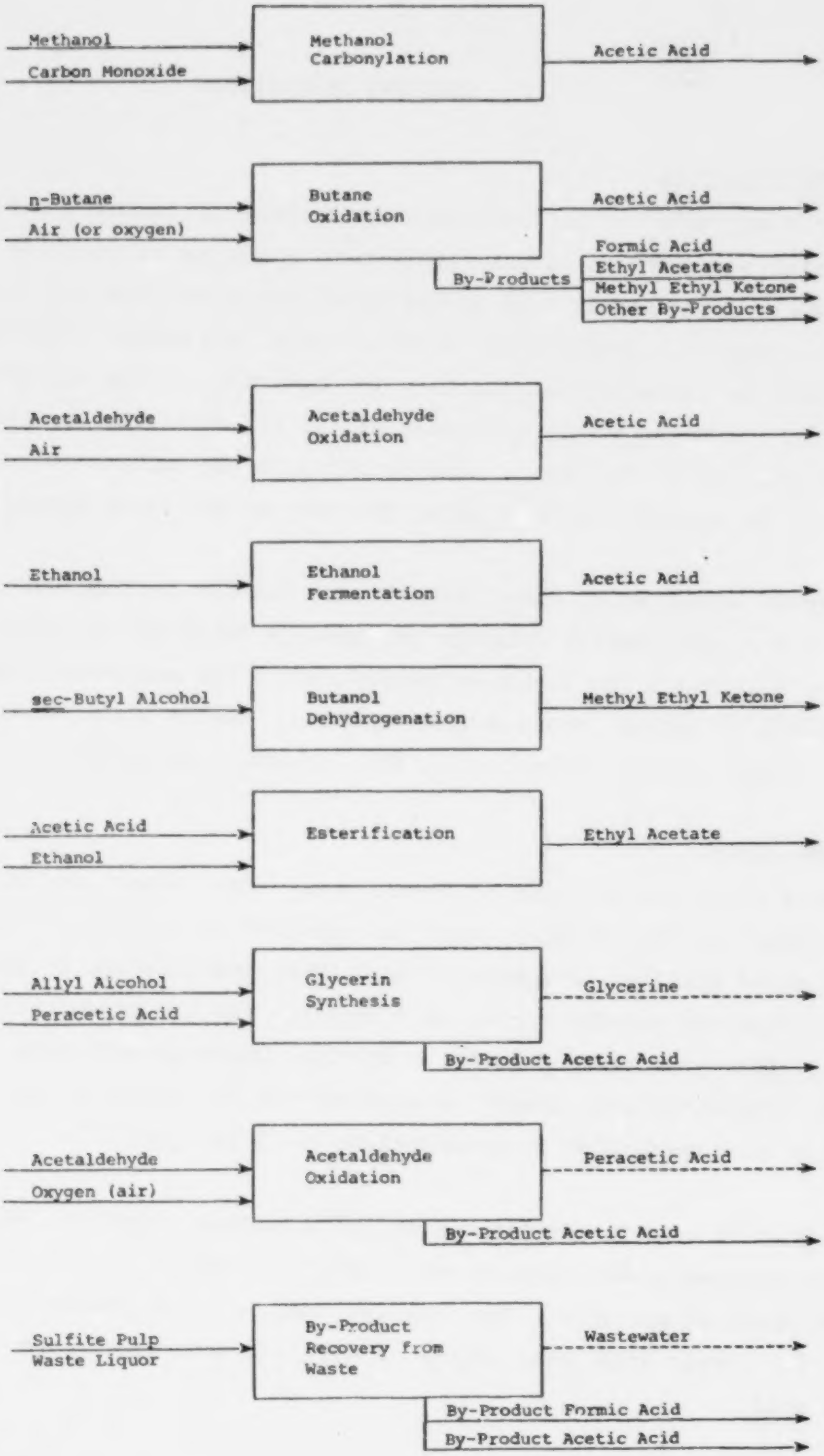
Methanol
Carbon Monoxide
Methanol Carbonylation
Acetic Acid
n-Butane
Air (or oxygen)
Butane Oxidation
Acetic Acid
By-Products
Formic Acid
Ethyl Acetate
Methyl Ethyl Ketone
Other By-Products
Acetaldehyde
Air
Acetaldehyde Oxidation
Acetic Acid
Ethanol
Ethanol Fermentation
Acetic Acid
sec-Butyl Alcohol
Butanol Dehydrogenation
Methyl Ethyl Ketone
Acetic Acid
Ethanol
Esterification
Ethyl Acetate
Allyl Alcohol
Peracetic Acid
Glycerin Synthesis
Glycerine
By-Product Acetic Acid
Acetaldehyde
Oxygen (air)
Acetaldehyde Oxidation
Peracetic Acid
By-Product Acetic Acid
Sulfite Pulp Waste Liquor
By-Product Recovery from Waste
Wastewater
By-Product Formic Acid
By-Product Acetic Acid

Fig. II-1. Production of Acetic Acid, Formic Acid, Ethyl Acetate, and Methyl Ethyl Ketone

Table II-1. Acetic Acid End Usage*

End Use	Acetic Acid Consumption for 1980 (%)
Vinyl acetate monomer	45
Cellulose acetate	25
Acetic esters	15
Terephthalic acid/dimethyl terephthalate	11
Miscellaneous	4

*See ref 1.

MEK is also used primarily as a solvent in such coatings as paints and varnishes, which are expected to boost its growth to about 5% per year.[4]

Domestic production capacities for acetic acid, formic acid, ethyl acetate, and MEK for 1980 are given in Table II-2.[1—9] Acetic acid production in 1979 was 1,510,000 Mg, or about 80% of capacity.[10] This capacity will be adequate for the projected growth until 1984.[1] The projected demand for formic acid, ethyl acetate, and MEK will not exceed the capacity to produce them until sometime after 1984.[2—10]

C. DOMESTIC PRODUCERS

Eight producers in 1980 were operating nine acetic acid plants employing three processes, plus three other plants that produced acetic acid as a by-product (see Table II-2 and Fig. II-1). Formic acid is produced as a by-product at two acetic acid plants that use the butane oxidation process (Celanese at Pampa, TX, and Union Carbide at Brownsville, TX) and at a Sonoco plant (Hartsville, SC) that recovers acetic acid from sulfite-pulp waste liquor.[1,2,5] MEK and ethyl acetate are produced both as by-products and from plants that may produce other ketones or esters, respectively.[6,7]

Acetic acid is produced by butane oxidation, by acetaldehyde oxidation, by methanol carbonylation, and until recently to a small extent by ethanol fermentation. With the recent completion of two new plants by Celanese and by USI Division of National Distillers (both of which use Monsanto's methanol carbonylation process) methanol carbonylation is the predominant process.[1,5] Wood distillation was the principal source of acetic acid in the United States for 75 years, but has not been used since 1973.[5,11]

Companies producing one or more of the products involved are as follows:

1. ARCO -- Produces MEK at Channelview, TX, reportedly from sec-butyl alcohol.[12]

2. Borden -- Produces acetic acid by a methanol carbonylation high-pressure process that uses BASF technology.[13]

3. Celanese -- Produces acetic acid by acetaldehyde oxidation at Bay City, TX, and Clear Lake, TX, by butane oxidation with air at Pampa, TX; started up during

Table II-2. Production Capacity for Acetic Acid, Formic Acid, Ethyl Acetate, and Methyl Ethyl Ketone[a]

		1980 Capacity (Mg/yr)			
Company	Location	Acetic Acid	Formic Acid	Ethyl Acetate	Methyl Ethyl Ketone
ARCO	Channelview, TX				29,500
Borden	Geismar, LA	52,000[b]			
Celanese	Bay City, TX	91,000			
	Clear Lake, TX	499,000			
	Pampa, TX	250,000	11,300[c]	32,000	40,800[c]
Eastman	Kingsport, TN	204,000		14,000	
	Longview, TX			18,000	
Exxon	Bayway, NJ				136,000
FMC	Bayport, TX	18,000[c]			
Monsanto	Texas City, TX	181,000			
	Springfield, MA			14,000[c]	
	Trenton, MI			7,000[c]	
Publicker	Philadelphia, PA	36,000[d]		9,000[d]	
Shell	Houston, TX				45,400
	Norco, LA				127,000
Sonoco	Hartsville, SC	3,000[e]	450[e]		
Union Carbide	Brownsville, TX	272,000	22,700[c]	36,000[c]	38,600[c]
	Taft, LA	18,000[c]			
USI	Deer Park, TX	272,000			
Total		1,896,000	34,450	130,000	417,300

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[a] See refs 1—9; some references give different capacities for the same location.

[b] Borden is increasing its capacity to 70,000 Mg/yr (ref 1).

[c] By-product from processes producing other products.

[d] Publicker acetic acid and ehtyl acetate plants have been shut down and are on standby (ref 1 and 3).

[e] Plant recovers acetic acid and formic acid from a waste stream; operated only to prevent water pollution 12 to 15 days/month (ref 9).

1978 a methanol carbonylation plant at Clear Lake, TX, that uses Monsanto technology. Produces MEK, formic acid, and ethyl acetate at Pampa.[4—7,13,14]

4. Eastman -- Produces acetic acid via acetaldehyde oxidation at Kingsport, TN, and ethyl acetate by esterification at Kingsport, TN, and from acetaldehyde at Longview, TX.[1,5]

5. Exxon -- Uses butanol dehydrogenation to produce MEK at Bayway, NJ; plans to expand capacity to 136,000 Mg/yr in 1977 have been reported.[4,7]

6. FMC -- Obtains acetic acid as a by-product from a process that produces glycerin at Bayport, TX.[5]

7. Monsanto -- Produces acetic acid at Texas City, TX, by their own methanol carbonylation process; produces ethyl acetate as a by-product at Springfield, MA, and Trenton, MI.[5,6,13]

8. Publicker -- Produced acetic acid by ethanol fermentation and ethyl acetate by ethanol esterification, both at Philadelphia, PA. Both plants are reported to be on standby.[1,3,6,13]

9. Shell -- Produces MEK by butanol dehydrogenation at Houston, TX, and Norco, LA.[4]

10. Sonoco -- Recovers acetic acid and formic acid as by-products of a process for removing acetic acid from the concentrated waste cooking liquor of their neutral sulfite semichemical pulping operation; the process is operated only for water pollution abatement and is located in Hartsville, SC.[9]

11. Union Carbide -- Produces acetic acid, formic acid, ethyl acetate, and MEK by butane oxidation with oxygen at Brownsville, TX; obtains acetic acid as a by-product from their peracetic acid process at Taft, LA; and produces ethyl acetate at South Charleston, WV, and Texas City, TX.[1—5,15]

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTIONS

A. INTRODUCTION

The three major processes for commerical production of acetic acid are carbonylation of methanol, oxidation of butane, and oxidation of acetaldehyde. Until recently the butane oxidation process, which produces several by-products, including MEK, ethyl acetate, and formic acid, had been the major source of acetic acid. However, more acetic acid is now produced by the methanol carbonylation process than by any of the other processes.[1,2] Very likely this process will be used for essentially all new, world-wide, acetic acid capacity. Monsanto claims that the manufacturing costs of their methanol carbonylation process are lower than those for any other known acetic acid process.[3—5]

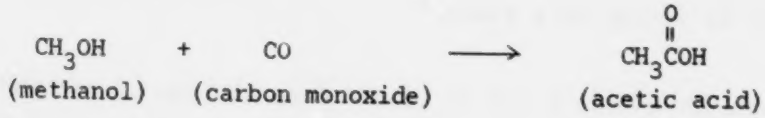
Ethanol fermentation is reported to have been used by Publicker for producing acetic acid, but no data are available on this process.[5]

The butanol dehydrogenation process for producing MEK and the esterification of acetic acid process for producing ethyl acetate are also covered in this section.

B. METHANOL CARBONYLATION FOR PRODUCTION OF ACETIC ACID

1. Basic Process

Acetic acid is produced by the continuous liquid-phase catalytic reaction of methanol and carbon monoxide:



$$\underset{\text{(methanol)}}{CH_3OH} + \underset{\text{(carbon monoxide)}}{CO} \longrightarrow \underset{\text{(acetic acid)}}{CH_3\overset{\overset{O}{\|}}{C}OH}$$

The catalyst used by Monsanto is a rhodium and iodine system that is very active and very selective at 200°C and 1.6 MPa. Water and other impurities formed by the reversible side reactions are recycled to the reactor. The main by-product comes from the water-gas reaction:

$$\underset{\text{(carbon monoxide)}}{CO} + \underset{\text{(water)}}{H_2O} \longrightarrow \underset{\text{(carbon dioxide)}}{CO_2} + \underset{\text{(hydrogen)}}{H_2}$$

Only small amounts of by-product are formed in the Monsanto process, which is represented in Fig III-1.[3,4]

Carbon monoxide (Stream 1), which has been separated from synthesis gas or some other nearby source, and methanol (Stream 2) are fed to the reactor system. The crude acetic acid (Stream 3) from the reactor system is fed to the light-ends column in the purification section. Wet acetic acid (Stream 4) is taken off as a sidestream and sent to the drying column, the light ends (Stream 5) go overhead and are recycled to the reactor system, and the heavy bottoms (Stream 6) also are recycled to the reactor system. In the drying column all the water and some acetic acid go overhead as wet acetic acid (Stream 7), which is recycled to the reactor system; dry acetic acid (Stream 8) is removed as bottoms and sent to the product column. Small quantities of propionic and acetic acid (Stream 9) are removed from the dry acetic acid in the product column and sent to an incinerator. The product column overhead (Stream 10) goes to the finishing column, where purified acetic acid (Stream 11) is removed as a sidestream and sent to storage. The finishing column overheads (Stream 12) and bottoms (Stream 13) are recycled to the process, resulting in a 99% yield of acetic acid based on methanol.[3]

The light ends (Vent A) vented from the reactor system and the vent gases (Vent B) from the column vents are combined and sent to a proprietary scrubber system, considered part of the process and not a control device, where essentially all the light material (Stream 14) is removed and recycled to the reactor system. The scrubber system is vented to a flare.[3]

Storage emission sources (Vents C and D) result from storage of methanol and acetic acid. Handling emissions (Vents E and F) result from loading of acetic acid into railroad tank cars and into barges.

Fugitive emissions (G) occur when leaks develop in valves or in pump or compressor seals. When process pressures are higher than the cooling water pressure, VOC can leak into the cooling water and escape as fugitive emissions from the cooling tower.

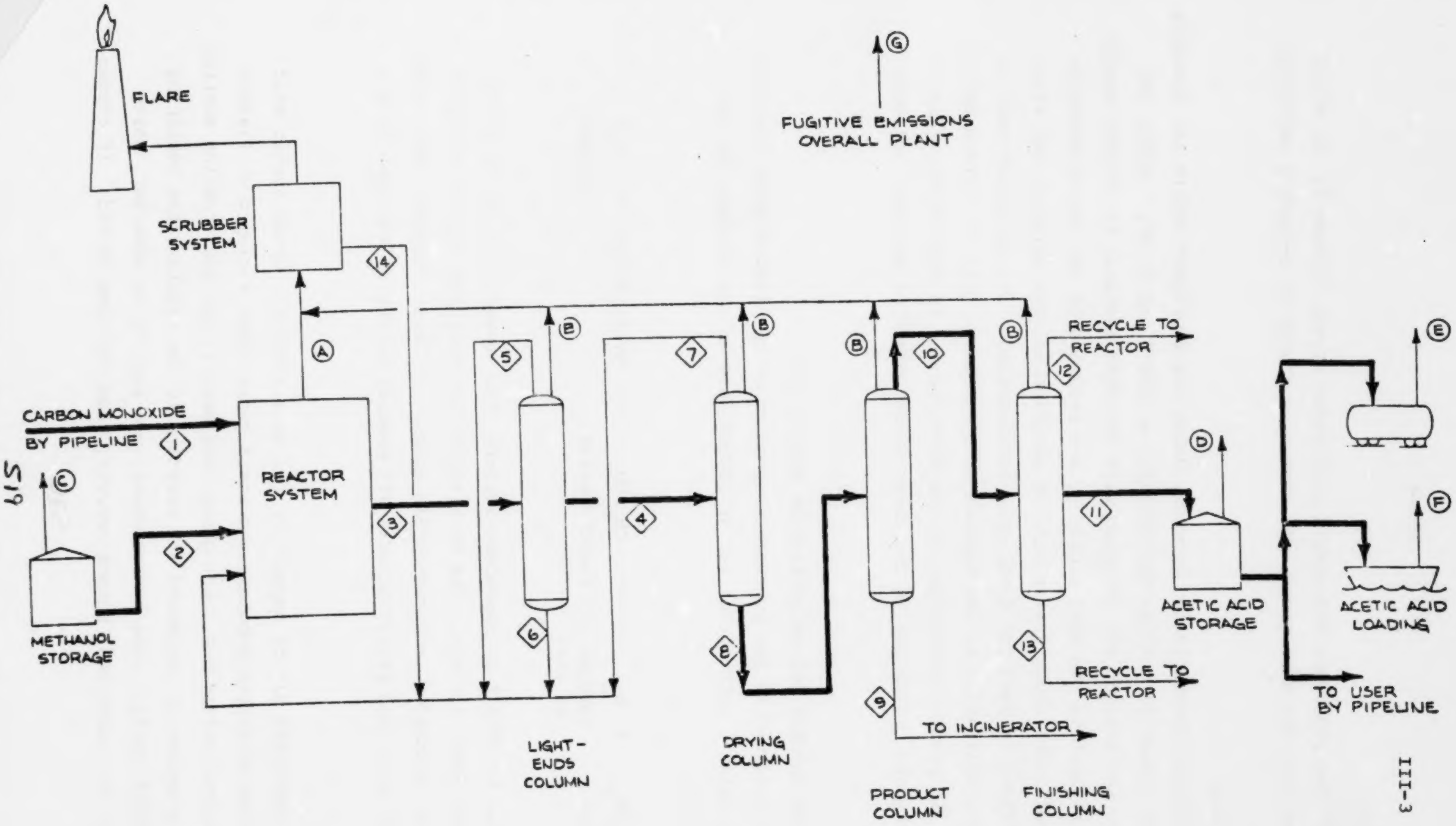

FLARE
SCRUBBER SYSTEM
FUGITIVE EMISSIONS OVERALL PLANT
G
14
A
B
5
7
B
B
10
B
RECYCLE TO REACTOR
12
E
CARBON MONOXIDE BY PIPELINE
1
REACTOR SYSTEM
D
C
3
4
11
F
2
METHANOL STORAGE
6
8
13
ACETIC ACID STORAGE
ACETIC ACID LOADING
RECYCLE TO REACTOR
9
TO USER BY PIPELINE
TO INCINERATOR
LIGHT-ENDS COLUMN
DRYING COLUMN
PRODUCT COLUMN
FINISHING COLUMN

Fig. III-1. Process Flow Diagram for Acetic Acid by Methanol Carbonylation

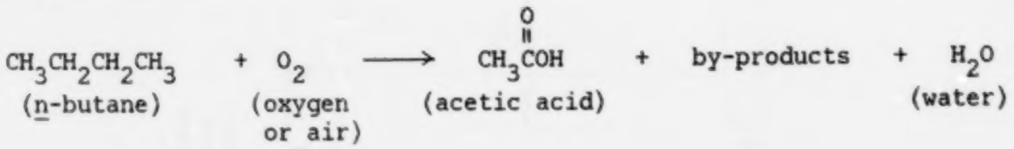
Incineration of the propionic and acetic acid waste stream (Stream 9), in which VOC are emitted with the flue gases, can also be a source of secondary emissions.

2. Process Variation

In the BASF methanol carbonylation process, which was developed before the Monsanto process, cobalt iodide is used as the catalyst at 250°C and 52 MPa. After the light ends from the reactor are scrubbed with the feed methanol to recover methyl iodide, they are sent to the fuel supply or are returned to the carbon monoxide separation plant. The crude acetic acid is purified in five columns, and azeotropic distillation is used for final acid purification. The entrainer used in the azeotropic distillation is the mixture of by-products that are formed during the reaction. By-product production in the BASF process is much higher than in the Monsanto process, resulting in the lower yield, based on methanol, of only 90%.[6—8]

C. BUTANE OXIDATION PROCESS FOR PRODUCTION OF ACETIC ACID

Acetic acid is produced as the predominant product of the liquid-phase catalytic oxidation of *n*-butane, with either air or oxygen used as the oxidant, by the following reaction:



$$\underset{\text{(n-butane)}}{CH_3CH_2CH_2CH_3} + \underset{\text{(oxygen or air)}}{O_2} \longrightarrow \underset{\text{(acetic acid)}}{CH_3\overset{\overset{O}{\|}}{C}OH} + \text{by-products} + \underset{\text{(water)}}{H_2O}$$

The catalyst can be cobalt or manganese acetate, the temperature 150 to 225°C, and the pressure about 5.5 MPa. The by-products are many and include alcohols, ketones, esters, aldehydes, and carboxylic acids. Of these, ethanol, MEK, ethyl acetate, formic acid, and propionic acid are usually recovered and used or are sold.[9,10]

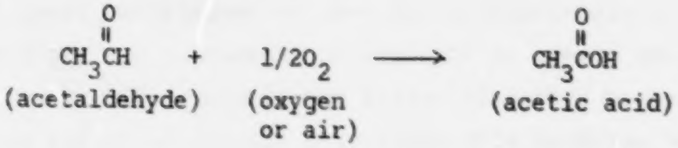
n-Butane and compressed air or oxygen are fed to a reactor. Crude acetic acid is separated from unreacted *n*-butane and inert gases, then stripped or flashed to remove dissolved butane and inert gases, and sent to the purification section. The unreacted *n*-butane is condensed and recycled to the reactor; the remaining inert gases, which contain some hydrocarbons, are sent to an absorber, which may use gas oil for additional butane recovery, and are then vented. If oxygen is used, refrigerated condensers may be adequate to recover the butane because of the reduced flow of inert gases.[5,9,11,12]

The low-boiling organics are separated from the crude acetic acid by conventional distillation. Azeotropic distillation is used to dry and purify the crude acetic acid. Recovery and purification of the various by-products require several distillation columns and involve extractive distillation or azeotrope breakers or both. Large amounts of liquid organic wastes are burned in boilers to recover their heat values. The aqueous waste is usually treated before being discharged.[9]

Process emissions are the vent gases from the reactor, which contain the nitrogen from the air when it is used to supply the oxygen, and the vent gases from the several distillation columns. The sources of storage and handling, secondary, and fugitive emissions are similar to those for the methanol carbonylation process, but the emissions may be significantly higher because of the many more volatile by-products produced.[9]

D. ACETALDEHYDE OXIDATION PROCESS FOR PRODUCTION OF ACETIC ACID

Acetic acid is made by the catalytic liquid-phase oxidation of acetaldehyde as shown by the reaction



$$\underset{\text{(acetaldehyde)}}{CH_3\overset{\overset{O}{\|}}{C}H} + \underset{\text{(oxygen or air)}}{1/2O_2} \longrightarrow \underset{\text{(acetic acid)}}{CH_3\overset{\overset{O}{\|}}{C}OH}$$

There are several variations to the process. The catalyst may be manganese or cobalt acetate and the reaction carried out in a large excess of acetic acid in a continuous reactor. Temperatures may range from 55 to 80°C and pressures from atmospheric to 520 kPa. Air or oxygen may be used as the oxidant, and ethanol may be mixed with the acetaldehyde feed and the two components oxidized together.[5,6,9]

Acetaldehyde and air or oxygen or oxygen-enriched air are fed to the reactor. Both a liquid and a gaseous stream leave the reactor. The gaseous stream is cooled and scrubbed several times with dilute acid and then with water to recover the organics, and the inert gases and unrecovered organics are vented to the atmosphere. The liquid stream is sent to the purification section, where unreacted acetaldehyde is removed by distillation and then recycled to the reactor. The dilute acetic acid is then distilled to remove water and impurities; the resultant dry purified acetic acid is sent to storage.[9]

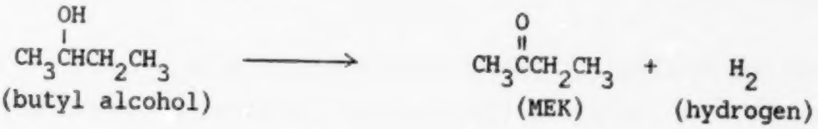
The process emissions are the scrubbed vent gases from the reactor and the vent gases from the distillation columns. The sources of storage and handling, secondary, and fugitive emissions are similar to those for the methanol carbonylation process.[9]

E. ETHANOL FERMENTATION PROCESS FOR PRODUCTION OF ACETIC ACID

No information is currently available on the ethanol fermentation or oxidation process to produce acetic acid.

F. BUTANOL DEHYDROGENATION PROCESS FOR PRODUCTION OF MEK

MEK is produced by the catalytic vapor-phase dehydrogenation of sec-butyl alcohol by the following reaction:



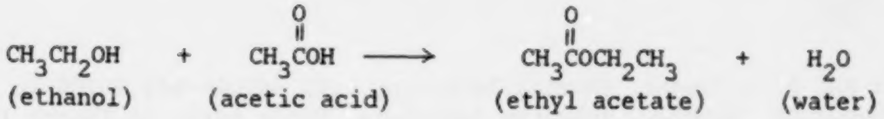
$$\underset{\text{(butyl alcohol)}}{CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_3} \longrightarrow \underset{\text{(MEK)}}{CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3} + \underset{\text{(hydrogen)}}{H_2}$$

The catalyst is zinc oxide or a zinc-copper alloy and the temperature range is 400 to 550°C. The reaction takes place at atmospheric pressure. The sec-butyl alcohol is vaporized and preheated before it enters the reactor. The reaction gases are condensed and may be scrubbed with water or a solvent to remove entrained MEK and sec-butyl alcohol from the hydrogen. The hydrogen can be used, burned in a furnace, or flared. The MEK is separated from the condensed reaction product by distillation, and unreacted sec-butyl alcohol is sent to a recovery step for recycle to the process.[6,11]

The only process emission source is vented gas from the distillation columns.[6] The sources of storage and handling, secondary, and fugitive emissions are similar to those previously described for other processes.

G. ESTERIFICATION PROCESS FOR PRODUCTION OF ETHYL ACETATE

Ethyl acetate is produced by the esterification of acetic acid and ethanol by the following reaction:



$$\underset{\text{(ethanol)}}{CH_3CH_2OH} + \underset{\text{(acetic acid)}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}OH} \longrightarrow \underset{\text{(ethyl acetate)}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_3} + \underset{\text{(water)}}{H_2O}$$

The catalyst employed is usually sulfuric acid and the process can be either continuous or batch.[6]

In the continuous process, acetic acid, excess ethanol, and sulfuric acid are mixed, passed through a preheater, and then sent to a reactor (esterifying column) held at 80°C and atmospheric pressure. The overhead distillate goes to a separating column, where an azeotrope of ethyl acetate, ethanol, and water goes overhead and is sent to a mixer for addition of water. The mixture goes to a decanter, where it separates into two layers. The bottom layer is mostly water and is recycled to the lower part of the separating column. The bottoms from the separating column are recycled to the bottom section of the esterifying column, where the alcohol is vaporized and a stream containing some sulfuric acid is removed and sent to waste. The top layer from the decanter is mostly ethyl acetate and goes to a drying column, where enough ethyl acetate is distilled overhead to remove the water and alcohol; this stream is recycled to the separating column. The bottoms of the drying column go to a finishing column, where ethyl acetate is separated overhead and sent to storage and the bottoms are sent to waste.[6]

Process emission sources can be the reactor condenser vent, the distillation column vents, and the decanter vent. The sources of storage and handling, secondary, and fugitive emissions are similar to those previously discussed for other processes.

H. ACETALDEHYDE PROCESS FOR PRODUCTION OF ETHYL ACETATE

Ethyl acetate is also produced from acetaldehyde. No data are currently available on the process or its emissions.[13,14]

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

A. INTRODUCTION

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

Table IV-1[1—16] summarizes the estimates of uncontrolled process emissions from the major processes producing acetic acid, by-product formic acid, ethyl acetate, or methyl ethyl ketone. These estimates do not include emissions from storage and handling, fugitive, or secondary sources. They are based on data from industry or from theory, whichever is the better available source, and are not representative of actual data from any specific plant. Storage and handling, fugitive, and secondary emissions for the entire synthetic organic chemicals manufacturing industry are covered by separate EPA documents.

B. METHANOL CARBONYLATION PROCESS FOR ACETIC ACID

The process flow diagram for the production of acetic acid by the methanol carbonylation process, given in Fig. III-1, was taken from the literature and represents the Monsanto process.[1—3] Both the reactor vent gases (Vent A) and the distillation vent gases (Vents B) are sent through the scrubber system and then to the flare. No data are available on the flow or composition of the gases from vent A or B. The stream to the flare consists of methane, nitrogen, carbon dioxide, carbon monoxide, and hydrogen.[4]

The data on uncontrolled emissions from the (older) BASF high-pressure process used by Borden are either not available or are confidential.[5] Estimates of the composition and flow of the vent gases from the reactor off-gas scrubber and from the light-ends distillation column, based on a theoretical material balance

Table IV-1. Estimates of Uncontrolled VOC Emissions from Processes Producing Acetic Acid, Methyl Ethyl Ketone, and Ethyl Acetate

			VOC Emissions	
Process	Product or By-Products	Capacity (Mg/yr)	Ratio (g/kg)[a]	Rate (kg/hr)
Methanol carbonylation	Acetic acid	250,000	2[b]	57[b]
Butane oxidation[c]	Acetic acid	250,000		
	Methyl ethyl ketone	40,000		
	Ethyl acetate	30,000		
	Formic acid	10,000		
Total for butane oxidation		330,000	38[d]	1400
Acetaldehyde oxidation	Acetic acid	200,000	6.9	160
Butanol dehydrogenation	Methyl ethyl ketone	100,000	1.2	14
Ethanol esterification	Ethyl acetate	10,000	0.3	0.3

[a] g of emissions per kg of product produced.

[b] Based on estimated VOC emissions from Monsanto process as reported by Monsanto (see ref 15).

[c] With oxygen; VOC emissions from the butane oxidation with air process are estimated by Celanese to be about three times higher (see ref 16).

[d] g of emissions per kg of total product mix produced.

for the BASF process calculated by S. Takaoka,[6] are given in Tables IV-2 and IV-3. These estimates are not meant to represent the emissions from any actual plant.

The estimate given in Table IV-1 for uncontrolled process emissions is based on estimates from Monsanto.[15] The incineration of the heavy ends is a potential source of secondary VOC emissions; however, no data are available on their amount or on the amounts of fugitive or storage and handling emissions.

C. BUTANE OXIDATION PROCESS FOR ACETIC ACID

The sources of emissions from butane oxidation processes include the butane recovery vents and purification vents. Table IV-4 gives the composition of the uncontrolled emissions from the refrigerated condensers used to recover butane in an oxygen-based butane oxidation plant.[7] The uncontrolled emissions from the distillation columns in the purification section of the same plant are estimated to contain 0.2 g of VOC per kg of total product mix produced by the plant. Some components in the purification vent gases include methyl acetate, acetone, methyl formate, acetaldehyde, methanol, ethyl acetate, butane, ethane, methane, other organics, carbon dioxide, carbon monoxide, and nitrogen.[8] The temperatures of the vent streams were not included in the available data. Available data on the emissions from the air-based butane oxidation process are difficult to interpret and incomplete; so no estimate was made of the VOC emissions. The estimate of uncontrolled emissions shown in Table IV-1 are for an oxygen-based butane oxidation process.

D. ACETALDEHYDE OXIDATION FOR ACETIC ACID

The total process emissions for a process based on acetaldehyde oxidation with air to produce acetic acid include the inert gases from the air with unrecovered organics from the reaction section plus the vent gases from the purification section. Table IV-5 gives the composition of the vent gases from the reaction section.[9] The total VOC emissions were estimated based on a weighted average of reported emissions from two plants (see Table IV-1). The VOC emitted are acetaldehyde, ethanol, ethyl acetate, ethyl formate, and n-propyl acetate. An analysis of the data shows that the ratio of VOC emission from the reaction section to the product produced varies with the production rate; one plant reports that when it operates near capacity the VOC emission ratio is twice that shown in Table IV-1.[9,10]

Table IV-2. Estimated Composition of Gas from Reactor Off-Gas Scrubber Vent in a BASF Methanol Carbonylation Plant Producing Acetic Acid[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
Methanol	3.5	12.9
Light ends	0.6	2.1
Total VOC	4.1	15
Hydrogen	1.5	5.5
Carbon monoxide	54	204
Carbon dioxide	37	141
Methane	3.4	12.8
Total	100	378

[a] Based on a theoretical material balance (see ref 6).

[b] g of emissions per kg of acetic acid produced.

Table IV-3. Estimated Gas Composition of Light-Ends Distillation Column Vent in a BASF Methanol Carbonylation Plant to Produce Acetic Acid[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
Hydrogen	0.28	0.079
Carbon monoxide	30	8.59
Carbon dioxide	67.5	19.3
Methane	2.22	0.63
Total	100	28.6

[a] Based on a theoretical material balance (see ref 6).

[b] g of emissions per kg of acetic acid produced.

Table IV-4. Composition of Vent Gas from Refrigerated Butane Recovery Condensers in Plant Using Butane Oxidation with Oxygen Process[a]

Component	Separator Condenser		Stripper Condenser	
	Composition (wt %)	Emission Ratio (g/kg)[b]	Composition (wt %)	Emission Ratio (g/kg)[b]
Butane	6.5	22	11	9
Ethane	0.8	3	1	0.8
Other organics	—	—	4	3
Total VOC	7.3	25	16	12.8
Methane	4.6	16	1	0.8
Carbon dioxide	56	190	80	65
Carbon monoxide	9	30	1	0.8
Nitrogen	8.1	26	1	0.8
Argon	15	53	1	0.8
Total	100	340	100	81

[a] See ref 7.

[b] g of emissions per kg of total product mix produced.

Table IV-5. Vent Gas Composition from Reactor Section in an Acetaldehyde Oxidation Plant[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
Acetaldehyde (VOC)	0.2	2
Nitrogen	96	960
Carbon dioxide	2.8	28
Oxygen	0.6	6
Carbon monoxide and methane	0.4	4
	100	1000

[a] See ref 9.

[b] g of emissions per kg of product produced.

E. BUTANOL DEHYDROGENATION PROCESS FOR MEK

The only process emissions from butanol dehydrogenation are the VOC in the noncondensables vented from the distillation column condensers in the purification section as the hydrogen produced in the reactor either is burned as fuel or is used elsewhere in the plant complex. The estimate of this emission (see Table IV-1) is based on information from three plants and on engineering judgement. The emissions may be continuous or periodic, depending on the method used to purge the noncondensables from the condensers.[11—13]

F. ESTERIFICATION PROCESS FOR ETHYL ACETATE

The estimate of VOC emissions from the esterification process to produce ethyl acetate (See Table IV-1) is based on limited data from one plant[14] and on engineering judgement. A relatively small amount of ethyl acetate is produced by this process; most is produced as a by-product.

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8. F. D. Bess, Union Carbide Corporation, letter dated Aug. 25, 1978 to J. A. Key, IT Enviroscience, Inc., with information on emissions from butane oxidation system at Brownsville, TX (on file at EPA, ESED, Research Triangle Park, NC).

9. J. A. Key, IT Enviroscience, Inc., *Trip Report for Visit to Celanese, Clear Lake, TX, Oct. 12, 1977* (on file at EPA, ESED, Research Triangle Park, NC).

10. J. C. Edwards, Tennessee Eastman Co., letter to EPA with information on Kingsport, TN, acetic acid plant, May 15, 1978.

11. C. N. Hudson, ARCO Chemical Co., letter to EPA with information on MEK unit in ARCO's Lyondell Plant at Channelview, TX, May 15, 1978.

12. J. A. Mullins, Shell Oil Co., letter to EPA with information on MEK plant at Deer Park, TX, June 22, 1978.

13. G. L. Otis, Exxon Chemical Co., letter dated June 7, 1978, to EPA with information on MEK unit in their Bayway, NJ, Chemical Plant.

14. J. C. Edwards, Tennessee Eastman Co., letter to EPA with information on Kingsport, TN, ethyl acetate plant, Aug. 11, 1978.

15. N. B. Gallozzo, Monsanto Plastics & Resins Co., letter dated Oct. 22, 1979, to D. R. Patrick, EPA, with comments on draft Acetic Acid Report (on file at EPA, ESED, Research Triangle Park, NC).

16. R. H. Maurer, Celanese Chemical Company, Inc., letter dated Oct. 10, 1979, to D. R. Patrick with comments on draft Acetic Acid Report (on file at EPA, ESED, Research Triangle Park, NC).

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V. APPLICABLE CONTROL DEVICES

A. INTRODUCTION

The control devices shown in Table V-1 were selected for new plants because either they are in use or they appear to be feasible based on a general knowledge of the emissions and of similar emissions from other processes controlled by such devices. The costs and cost effectiveness for these applications have not been determined.

B. METHANOL CARBONYLATION PROCESS FOR ACETIC ACID

The process emissions from the reactor off-gas scrubber system in the Monsanto process is controlled by a flare. Even though the scrubber system is part of the process and is not considered to be a control device, the distillation column vent gases may be sent to the scrubber system as a control technique.[1] Monsanto reports an estimate of controlled VOC emissions from the flare of 0.03 g of acetic acid emission per kg of acetic acid produced, with an estimated destruction efficiency of 98.5% for the flare.[2]

An emission reduction of 99% was used to calculate the controlled emissions from a flare used as a control device on the emissions from the off-gas scrubber and from all distillation vents (see Table V-1). This reduction is based on a flare that is designed so that the normal flow is greater than 10% of design.[3] The use of a flare to control emissions from a vacuum column, where air leaks may cause an explosive mixture in the flare or header system, must be examined carefully and proper precautions taken to prevent a hazardous condition.[4]

C. BUTANE OXIDATION PROCESS FOR ACETIC ACID

No control devices are given for a new butane oxidation process, because no new acetic acid plants are expected to use the butane oxidation process as it is very energy intensive.[5] See Appendix B for retrofit considerations for existing butane oxidation processes.

D. ACETALDEHYDE OXIDATION PROCESS FOR ACETIC ACID

An acetic acid and water scrubber was selected as a control device option for the process emissions from an acetaldehyde oxidation process producing acetic

Table V-1. Estimates of Controlled VOC Emissions from Processes Producing Acetic Acid, Methyl Ethyl Ketone, and Ethyl Acetate

Process	Product or By-Product	Capacity (Mg/yr)	Control Device	VOC Emission Reduction (%)	VOC Emissions	
					Ratio (g/kg)[a]	Rate (kg/hr)
Methanol carbonylation	Acetic acid	250,000	Flare	99	0.02	0.57
Butane oxidation[b]	Acetic acid	250,000				
	Methyl ethyl ketone	40,000				
	Ethyl acetate	30,000				
	Formic acid	10,000				
Total for butane oxidation		330,000				
Acetaldehyde oxidation	Acetic acid	200,000	Scrubber	99	0.069	1.6
Butanol dehydrogenation	Methyl ethyl ketone	100,000	Flare	99	0.012	0.14
Ethanol esterification	Ethyl acetate	10,000	None		0.3	0.3

[a] g of emissions per kg of product produced.

[b] See Appendix B for retrofit considerations for existing butane oxidation processes; no new butane oxidation plants are likely.

acid (see Table V-1). This option is based on the current use of such scrubbers to control the emissions from acetaldehyde oxidation processes that use air as the oxidant. A reduction efficiency of 99% (see Table V-1) was used to calculate the controlled emissions from this process based on reported data. A conceptual design of an acetic acid and water scrubber for this application has not been made nor have data been developed on costs or cost effectiveness.[6,7] The problems involved with retrofitting this control to an existing acetaldehyde process are discussed in Appendix B.

E. BUTANOL DEHYDROGENATION PROCESS FOR MEK

A flare was selected as an emission control device option for the vent gases from the purification section condensers. An emission reduction of 99% was used to calculate the controlled emissions (see Table V-1) based on such a flare that is designed so that the normal flow is greater than 10% of design.[3]

F. ESTERIFICTION PROCESS FOR ETHYL ACETATE

No control system has been identified for this process because the estimated emissions for the industry are small. The estimated controlled emissions are therefore the same as the uncontrolled emissions (see Table V-1). No control devices are used in the one plant for which data are available.[8]

G. REFERENCES

1. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Monsanto Co., Texas City, TX, Dec. 13, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

2. N. B. Galluzzo, Monsanto Plastics and Resins Co., letter dated Oct. 22, 1979, to D. R. Patrick, EPA, with comments on draft Acetic Acid Report (on file at EPA, ESED, Research Triangle Park, NC).

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7. J. C. Edwards, Tennessee Eastman Co., letter to EPA with information on Kingsport, TN, acetic acid plant, May 15, 1978.

8. J. C. Edwards, Tennessee Eastman Co., letter to EPA with information on Kingsport, TN, ethyl acetate plant, Aug. 11, 1978.

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VI. IMPACT ANALYSIS

A. ENVIRONMENTAL IMPACT

Table VI-1 shows the environmental impact of reducing VOC emissions by application of the described control systems (Sect. V) to typical new plants for production of acetic acid, methyl ethyl ketone, and ethyl acetate having the capacities indicated. The environmental impacts of controlling VOC emissions from storage and handling, fugitive, and secondary sources are not included in the estimates in Table VI-1 but are believed to be similar to those from other processes in the synthetic organic chemicals manufacturing industry.

The projected production rates for 1978 are 1,240,000 Mg for acetic acid, 74,100 Mg for ethyl acetate, and 244,000 Mg for MEK, all based on the reported 1977 production and estimated annual growth rate.[1—4] Formic acid production was not projected because it is produced only as a by-product and data are not available on emissions, if any, resulting solely from its recovery.[5] Table VI-2 lists the estimated current VOC emissions from each acetic acid process and for the methyl ethyl ketone and ethyl acetate processes. These estimates are based on the projected production of each product for 1978 adjusted by the fraction of total production capacity for each acetic acid process before the recent expansions and on an estimated current emission ratio to production for each process.

These estimates include emissions from the processes only, not those from storage and handling, secondary, or fugutive sources. Emissions from these sources are believed to be typical for the synthetic organic chemicals manufacturing industry. The water effluent from scrubbers may have an adverse environmental impact unless treated in a properly designed and operated wastewater treatment plant.

B. OTHER IMPACTS

Energy and control cost impacts have not been determined for the control devices selected in Section V.

Table VI-1. Environmental Impact of Controlled Typical Processes Producing Acetic Acid, Methyl Ethyl Ketone, and Ethyl Acetate

Process	Product or By-Products	Capacity (Mg/yr)	Control Device or Technique	VOC Emission Reduction[a] (%)	(Mg/yr)
Methanol carbonylation	Acetic acid	250,000	Flare	99	495
Butane oxidation[b]	Acetic acid	250,000			
	Methyl ethyl ketone	40,000			
	Ethyl acetate	30,000			
	Formic acid	10,000			
Total for butane oxidation		330,000			
Acetaldehyde oxidation	Acetic acid	200,000	Scrubber	99	1400
Butanol dehydrogenation	Methyl ethyl ketone	100,000	Flare	99	119
Ethanol esterification	Ethyl acetate	10,000	None		

[a] Impact of controlling process emissions; does not include storage and handling, fugitive, or secondary emissions.

[b] No control devices are given, as no new butane oxidation plants are likely; see Appendix B for retrofit considerations.

Table VI-2. Estimate of Current Industry Emissions from Processes Producing Acetic Acid, Methyl Ethyl Ketone, and Ethyl Acetate

Process	Product or By-Products	Control Device or Technique	1978 VOC Emissions (Mg)[a]
Methanol carbonylation	Acetic acid	Monsanto process	30[b]
Butane oxidation	Acetic acid	Refrigerated vent condensers and flare[d]	4400[c]
	Methyl ethyl ketone		
	Ethyl acetate		
	Formic acid		
Acetaldehyde oxidation	Acetic acid	Scrubber	880
Butanol dehydrogenation	Methyl ethyl ketone	Flare	22
Ethanol esterification	Ethyl acetate	None	10

[a] Emissions from the process only; does not include emissions from storage and handling, fugitive, or secondary sources.

[b] Emissions are from the BASF process; little VOC is emitted from the Monsanto process.

[c] The total industry emissions are estimated from the data for the butane oxidation with oxygen process only.

[d] Refrigerated vent condensers on separator condenser and purification section vents; flare on stripper condenser vent.

C. REFERENCES

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2. "Ethyl Acetate," Chemical Marketing Reporter 211(21), 9 (May 23, 1977).
3. "MEK," Chemical Marketing Reporter 210(26), 9 (Dec. 27, 1976).
4. "Manual of Current Indicators——Supplemental Data," pp. 201, 224, and 242 in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (October 1978).
5. "Formic Acid," Chemical Marketing Reporter 211(12), 9 (Mar. 21, 1977).

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Table A-1. Physical Properties of Acetic Acid*

Synonyms	Methane carboxylic acid, ethylic acid, glacial acetic acid
Molecular formula	$C_2H_4O_2$
Molecular weight	60.05
Vapor pressure	1.52 kPa at 20°C
Vapor specific gravity	2.07
Boiling point	117.9°C
Melting point	16.6°C
Density	1.0492 g/ml at 20°C/4°C
Water solubility	Infinite

*J. Dorigan _et al._, "Acetic Acid," p. AI-16 in _Scoring of Organic Air Pollutants, Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals A-C)_, MTR-7248, Rev. 1, Appendix I, MITRE Corp., McLean, VA (September 1976).

Table A-2. Physical Properties of Formic Acid*

Synonyms	Methanoic acid, hydrogen carboxylic acid
Molecular formula	CH_2O_2
Molecular weight	46.3
Vapor pressure	5.65 kPa at 25°C
Vapor specific gravity	1.59
Boiling point	100.8°C
Melting point	8.3°C
Density	1.2201 g/ml at 20°C/4°C
Water solubility	Infinite

*J. Dorigan *et al.*, "Formic Acid," p. AIII-16 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F-N)*, MTR-7248, Rev. 1, Appendix III, MITRE Corp., McLean, VA (September 1976).

Table A-3. Physical Properties of Ethyl Acetate*

Synonyms	Acetic ester, ethylacetic ester, ethyl etharate
Molecular formula	$C_4H_8O_2$
Molecular weight	88.10
Vapor pressure	12.3 kPa at 25°C
Vapor specific gravity	3.04
Boiling point	77.06°C
Melting point	-83.578°C
Density	0.8946 g/ml at 25°C/4°C
Water solubility	89 g/liter of H_2O

*J. Dorigan *et al.*, "Ethel Acetate," p. AII-234 in *Scoring of Organic Air Pollutants, Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals D-E)*, MTR-7248, Rev. 1, Appendix II, MITRE Corp., McLean, VA (September 1976).

Table A-4. Physical Properties of Methyl Ethyl Ketone*

Synonyms	2-Butanone, methyl acetone
Molecular formula	C_4H_8O
Molecular weight	72.12
Vapor pressure	12.85 kPa at 25°C
Vapor specific gravity	2.41
Boiling point	79.6°C
Melting point	-86.35°C
Density	0.8054 g/ml at 20°C/4°C
Water solubility	Infinite

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*J. Dorigan *et al.*, "Methyl Ethyl Ketone," p. AIII-192 in *Scoring or Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F-N)*, MTR-7248, Rev. 1, Appendix III, MITRE Corp., McLean, VA (September 1976).

EXISTING PLANT CONSIDERATIONS

To gather information for the preparation of this report four site visits were made to manufacturers of acetic acid. Trip reports have been cleared by the companies concerned and are on file at ESED in Durham, NC.[1—5] Some of the pertinent information concerning process emissions from these existing acetic acid plants is presented in this appendix. Other information is from letters to EPA from companies that produce acetic acid, MEK, or ethyl acetate in response to requests for information on process emissions from processes that produce those chemicals.[6—10] Also included is information received with comments on the draft Acetic Acid Report.[11,12]

A. CONTROLS AT EXISTING PLANTS

1. Monsanto, Texas City, TX

Acetic acid is produced by carbonylation of methanol by a low-pressure, liquid-phase process developed and commercialized by Monsanto and being licensed to other companies. The process consists of a reaction system, a scrubber system, and a distillation system. The emission from the scrubber system is the only process emission and goes to a flare. All the column accumulators in the distillation system are vented back to the scrubber system. The unit capacity is 350 million lb of acetic acid per year. The unit was completed in 1970 and there have been no major modifications made since that time.[1]

Monsanto reports the estimated controlled emissions from the flare to be the following:

Flare Effluent	Ratio (g/kg)[a]	Rate (g/sec)[b]
Carbon monoxide	0.356	2.25
Acetic acid	0.03	0.19

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[a] g of VOC per kg of product produced.

[b] Basis: nominal 50,000-lb/hr production rate.

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Monsanto estimates that halogen compounds also leave the flare at a rate of 1 to 2 lb/hr and that some VOC escapes the scrubber device to the flare. They

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also report that the flare vendor estimates destruction of VOC (acetic acid) at 98.5%; destruction of CO is estimated to be 99%.[11]

2. Borden, Geismar, LA

In the BASF high-pressure acetic acid process used by Borden at Geismar, LA, the reactor off-gas from the high-pressure separator is recycled to the process. The emissions from the off-gas scrubber that originate in the low-pressure separator are sent to a flare that also serves other processes. The emissions from the vents on the atmospheric distillation columns go through a series of scrubbers for recovery of organics. Chilled methanol is used in the final scrubber, with an estimated removal efficiency of 80%, and is used as an emission control device before the vent gases are released to the atmosphere. The emissions from the liquid-ring vacuum pump serving the two vacuum distillation columns go directly to the atmosphere. The Borden plant was built in about 1964, and no major modifications have been made since then.[2]

3. Union Carbide, Bronsville, TX

Acetic acid is produced by the liquid-phase oxidation on n-butane with oxygen. By-products of the reaction that are recovered at the Brownsville plant are ethanol, methyl ethyl ketone, ethyl acetate, and formic acid. Acetic anhydride is produced from acetic acid by a ketene process licensed from Tennessee Eastman. The Brownsville plant was originally built in 1950 by Carthage Hydrocol Co. to produce gasoline and other fuels and chemicals from natural gas, but was shut down in 1953. Standolind Oil and Gas Co. acquired the plant and made additions and modification to it; however, because of poor economics, it was shut down in 1957. Union Carbide purchased the facilities and converted the equipment to produce acetic acid, etc., in 1961, and added one new still. The plant was expanded in 1965.

Process emissions from the butane oxidation with oxygen process are controlled by refrigerated vent condensers and a flare. A refrigerated vent condenser is used to control the VOC in the vent gases from the separator condenser and has a reduction efficiency of 68%; the temperatures of the streams in and out of the control device are not currently available. The flare is used as the control device for the VOC in the emissions from the stripper vent condenser and is sized to handle flows from other sources. Very low pressure ratings on some vessels have prevented use of the flare on their vents. Refrigerated vent condensers are used as control devices on the vents from the crude separation columns and the topping columns in the purification section. The available data on the controlled emissions from these vent condensers show wide variations, believed to be due to erratic operation of the refrigeration equipment at the time that the data were taken. The temperatures of the streams to and from the condensers are not currently available. An estimate of the controlled emissions was made based on the emissions when the refrigeration equipment was believed to be operating normally. The VOC reduction was estimated at 60% (see Table B-1). The other columns in the purification section are not normally vented.[3,4]

4. Celanese, Clear Lake, TX[5]

The acetic acid unit was constructed in 1969—1970 by Brown and Root to a Celanese design. No major modifications have been made since the unit was constructed. The process used involves the catalytic air oxidation of liquid acetaldehyde. The off-gases from the reactor are largely nitrogen and carbon dioxide from the air fed to the reactor and are scrubbed with water in the reactor vent scrubber to recover product and raw material before they are discharged to the atmosphere. The composition and flow of these emissions (waste gas 1) in lb/1000 lb of acetic acid produced are given in Table B-2 for two different production rates.

The reaction product is purified by distillation, and the gases from the vents on the distillation column condensers and accumulators are collected and sent through the unit vent scrubber. The composition and vent rate in scfm are given in Table B-2 as waste gas 2.

The reactor vent scrubber was not designed to control pollution but to recover product and raw material for economic reasons. The top temperature is 55°F in the winter and 70°F in the summer. No acetic acid is detectable in the emissions from the reactor vent scrubber except during an upset. The composition of waste gas 1 was determined by gas chromatography and is on a dry basis although the stream is actually saturated.

The unit vent scrubber is an emission control device, with the top temperature 80°F in the winter and 95°F in the summer. No data are available on the composition, flow, etc., of the vent stream into the unit vent scrubber.

Table B-1. Estimates of Controlled VOC Emissions from the Union Carbide Butane Oxidation with Oxygen Process[a]

Source	Uncontrolled VOC Emission Ratio (g/kg)[b]	Control Device	VOC Emission Reduction (%)	Controlled VOC Emission Ratio (g/kg)[b]
Separator condenser vents	25	Refrigerated vent condensers	68	8
Stripper condenser vents	12.8	Flare	95	0.6
Purification section vents	0.2	Refrigerated vent condensers	60	0.08
Total	38			8.68

[a] See refs 3 and 4.

[b] g of emissions per kg of total product mix produced.

Table B-2. Celanese Acetic Acid Source Emissions[a]

	Waste Gas 1				Waste Gas 2[b]
	Production Rate A		Production Rate B		Production Rate A and B
Component	(wt %)	(lb/1000 lb)	(wt %)	(lb/1000 lb)	(wt %)
N_2	95.9	1075.7	97.3	1022.2	96.3
H_2O					3.2
O_2	0.6	6.0			
CO_2	2.8	31.3	2.7	28.8	
C_2H_4O	0.3	3.7	Trace	0.3	0.5
$CO + CH_4$	0.4	4.6			
	100.0	1121.3	100.0	1051.3	

[a] See ref 5.

[b] Vent rate, ∿50 scfm.

5. Tennessee Eastman, Kingsport, TN

The acetaldehyde oxidation acetic acid process uses a scrubber that employs acetic acid and water to remove VOC from the reactor off-gases, with a reported efficiency of 99%, before they are released to the atmosphere. Tennessee Eastman considers the acetic acid and water scrubber as an integral part of the process and not as an air pollution control device. The emissions from this scrubber are as follows:

Flow: 200 lb/hr
Composition: 97.4—89.4% N_2*
2.5% CO_2
1500 ppm CO
1 ppm acetaldehyde
1 ppm ethyl alcohol
1 ppm ethyl acetate
18 ppm ethyl formate
0—8% O_2*
Temperature: 40°F

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*Based on engineering estimates; all other based on gas chromatography analysis.

One column vent has a water-cooled vent condenser as the control device, with an estimated reduction efficiency of 99% for removing n-propyl acetate.[6]

6. ARCO, Channelview, TX

The process for dehydrogenation of secondary butyl alcohol (SBA) to produce MEK uses a smokeless flare as an emission control device.[7]

7. Shell, Deer Park, TX

MEK is produced by dehydrogenation of secondary butyl alcohol. The uncontrolled emissions from the purification section are as follows:

Accumulator vent from the SBA Recovery Column that processes H_2 scrub water; vent gas routed to flare 5.

Flow:	0.0012 lb/lb of MEK production	
Composition (wt %):	SBA, 73	
	H_2O, 27	
Temperature:	190°F	

The flow was determined by vane anemometers and the composition by design calculations.

Accumulator vent gas from the MEK dehydration column is routed to flare 6; flow occurs during hot weather or for about 4 months/yr.

Flow:	0.0035 lb/lb of MEK production	
Composition (wt %):[a]	$C_2^{=}$-$C_6^{=}$	55.2
	C_1°-C_6°	2.5
	IPE	15.1
	DMK	4.1
	MEK	5.0
	H_2, N_2, O_2, CO_2	18.1
Temperature:	130°F	

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[a] Determined by analysis of vent and flow measurement.

Control devices used are smokeless flares 5 and 6. Each flare serves several other process facilities in the Deer Park manufacturing complex. The flares are sized to handle large flows under emergency conditions. Streams from the above vents each constitute a very small percentage of the smokeless capacity of each flare.[8]

8. **Exxon, Bayway, NJ**

Two process emission points in the MEK process are described below:

a. The distillation tower is operated under positive pressure, with SBA/MEK-rich overhead vapors passing through two stage condensers and recycled to the process. The noncondensables that collect in the overhead condensers are periodically purged to two parallel blowdown drums that are integrated with other processes. The vapors are contacted with cooling water in the blowdown drums. Noncondensable vapors from these drums are vented. The average calculated atmospheric emissions are about 1 lb/ hr of C_4 hydrocarbons at ambient temperature.

b. The dehydration tower is also operated under positive pressure. The overhead vapors pass through three stage condensers, with condensed vapors recycled to the process. The noncondensables that collect in the overhead condensers are periodically vented to the atmosphere. The average calculated atmospheric emission is about 5 lb/hr of MEK at 100°F. The emission control device on vent 1 is a type of water scrubber, consisting of two parallel, vertical blowdown drums with internal horizontal baffles and countercurrent water flow, to condense some VOC from the column condenser vents and from other sources.[9]

9. Tennessee Eastman, Kingsport, TN

Ethyl acetate is produced from acetic acid and ethyl alcohol. The emissions from the columns and the extractor are as follows:

Stream A
Flow: 4.5 lb/hr
Composition (wt %):[a] 86.4 nitrogen
11.1 ethyl acetate
0.4 carbon monoxide
0.3 ethyl alcohol
0.02 methane
0.01 acetaldehyde, acetic acid, and methyl acetate
Temperature: Ambient

Stream B
Flow: Not detectable
Composition: No data available
Temperature: Ambient

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[a] Based on gas chromatography analysis.

No control devices are used.[10]

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

Another difficulty may be the possibility of overpressuring existing equipment because of pressure drop through an emission control device such as a flare, carbon adsorption, or scrubber. When water scrubbing is used, the scrubbing water must be treated. If there is no treatment plant or if it is too small, the cost of treatment of a large amount of scrubbing water from a water scrubber retrofitted to an existing process can be very expensive.[13]

C. REFERENCES

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2. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Borden Chemical Co., Geismar, LA, Mar. 3, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

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4. F. D. Bess, Union Carbide Corporation, letter dated Aug. 25, 1978 to J. A. Key, IT Enviroscience, Inc., with information on emissions from butane oxidation system at Brownsville, TX (on file at EPA, ESED, Research Triangle Park, NC).

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REPORT 10

WASTE SULFURIC ACID TREATMENT FOR ACID RECOVERY

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February 1981

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^1
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^2
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^4
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^1
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^9	1 Gg = 1 X 10^9 grams
M	mega	10^6	1 Mg = 1 X 10^6 grams
k	kilo	10^3	1 km = 1 X 10^3 meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. INTRODUCTION

Although sulfuric acid is an inorganic chemical, it is used by the synthetic organic chemicals manufacturing industry (SOCMI) in the production of synthetic organic chemicals as an acidulating agent, a catalyst, or a dehydrating agent or in some similar function. In many of these processes substantial quantities of spent sulfuric acid and/or sulfate salts contaminated with volatile organic compounds (VOC) are generated. The spent acids may be used in other operations, or they may be processed for recovery of sulfuric acid for sale, for use in other operations, or for recycle to the SOCMI process that generated the spent acid. The spent-acid recovery process may be part of a sulfuric acid plant that is either off-site or at the same site where the spent acid is produced, or it may be a reconcentration process that is integrated with the spent-acid producing process.[1] This report covers in abbreviated form the recovery of sulfuric acid from spent acids and sludges that contain VOC and that are generated in producing synthetic organic chemicals.

B. SULFURIC ACID USE IN SOCMI

In 1978, 36 Tg (36 million metric tons) of sulfuric acid were produced in the United States, 90% of this acid was used for the production of fertilizers nad other inorganic chemicals. In these processes the acid either becomes part of the product or remains as a nonrecoverable by-product. The remaining 10 to 12% of the domestic sulfuric acid production not used in the inorganic chemical industry is consumed by the petroluem, petrochemical, and organic chemical industries.[2]

The 1976 Organic Chemical Producers Data Base reports 1270 units producing SOCMI chemicals in the United States.[3] Of the 378 SOCMI chemicals sulfuric acid can be used in as many as 57 chemicals at some stage in their manufacture.[4--6] Table II-1 shows the SOCMI chemicals in which sulfuric acid can be used. Since about 15% of the SOCMI chemicals use sulfuric acid, it is assumed that 15% of the SOCMI production units (190 units) use sulfuric acid.

These 190 organic-chemical-producing units consume around 5% of the total domestic production of sulfuric acid, or 1.9 Tg/yr (100% sulfuric acid basis).[2]

Table II-1. List of SOCMI Chemicals Produced by Processes That Can Use Sulfuric Acid[a]

Chemical
Acetone
Acetonitrile
Acetophenone
Acrylamid
Acrylic acid and esters
Acrylonitrile
Anthraquinone
Benzene disulfonic acid
Benzene sulfonic acid
n-Butyl acetate
n-Butyl acrylate
sec-Butyl alcohol
t-Butyl alcohol
t-Butyl amine
Cellulose acetate
o-Chloro nitrobenzene
p-Chloro nitrobenzene
m-Cresol
b-Cresol
p-Cresol
Diethyl sulfate
n,*n*-Dimethyl aniline
Dimethyl sulfate
Dinitrobenzoic acid
Dinitrotoluene
Dioxane
Ethyl acetate
Ethyl acrylate
Ethylene glycol
Hydrogen cyanide
Isobutyl acetate
Isobutylene (di and tri)
Isopropyl acetate
Methacrylic acid
Methyl acetate
Methyl acetoacetate
Methyl chloride
Methyl methacrylate
Morpholne
1-Naphthalene sulfonic acid
2-Naphthalene sulfonic acid
1-Naphthol
2-Naphthol
Neopentansic acid
Nitrobenzene
m-Nitrobenzoic acid
Nitrotoluene
Octyl phenol
Phenol
Phenol sulfonic acid
Phthalic anhydride
Propylene chlorohydrin
Sulfanilic acid
Tetra chlorophthalic anhydride
Toluene sulfonic acid
p-Toluene sulfonic chloride
Xylenols

[a] See refs 4—6.

It is reported that production of alcohols (predominantly isopropyl and sec-butyl alcohols) used 964 Gg, or about 2.7%, of the 1978 consumption of 36 Tg of sulfuric acid (100% basis).[1] This means that about 940 Gg of sulfuric acid (100% basis) was consumed by other SOCMI processes. Of the 964 Gg of sulfuric acid used in the production of alcohols, 818 Gg was reconcentrated and used on-site, leaving 146 Gg of waste acid that was used in other processes off-site, that formed a sludge that was reprocessed by sulfuric acid manufacturers, or that was lost. As a result, an equivalent amount of virgin acid was actually consumed.[1] Therefore 5.6 times the amount of virgin acid consumed was reconcentrated and recycled on-site. If this ratio holds for other SOCMI products, then a total of about 6.1 Tg of sulfuric acid (100% basis) was reconcentrated.

C. REFERENCES*

1. R. E. Davenport et al., "Sulfuric Acid," pp. 780.1000A—G and 780.1001A—780.1004C in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (August 1979).

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6. Morrison and Boyd, Organic Chemicstry, Allyn and Bacon, Inc., 1975.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. SULFURIC ACID RECOVERY TECHNIQUES

A. INTRODUCTION

Three principal methods of recovering sulfuric acid are not in general use: (1) spent acid regeneration, (2) indirect evaporation, and (3) direct evaporation. The spent-acid regeneration process invovles the decomposition of the acid at temperatures of 1000 to 1150°C to produce sulfur dioxide, oxygen, and water vapor. The sulfur dioxide is oxidized to sulfur trioxode, which is absorbed to produce highly concentrated sulfuric acid or oleum. The two other processes, direct and indirect evaporation, are used to concentrate dilute sulfuric acid. The indirect-evaporation process uses steam or other heating media in indirect heaters to vaporize water and organics from the acid. The direct-evaporation process uses hot flue gases directly in contact with the spent acid to remove water and VOC.

This section describes the three processes used for spent sulfuric acid treatment, along with some advantages and disadvantages of each process.

B. DIRECT EVAPORATION

1. Drum Concentrator

The recovery of sulfuric acid by direct evaporation involves contacting hot gases, usually from combustion of fuel, with the spent acid to evaporate water and impurities. Figure III-1 is a flow diagram for a process developed in the 1920s by Chemico, now a division of Barnard and Burk, Inc., to recover sulfuric acid from oil refinery spent acids and later used to recover sulfuric acid from spent acid from high-explosive manufacture and from organic intermediates nitration processes. The evaporation is performed in a drum concentrator——a horizontal cylindrical steel vessel lined with heavy sheet lead and acid-proof brick and divided by brickwork into two compartments. The hot gases flow countercurrent to the acid flow through the drum concentrator and a cooling drum.[1,2]

The spent acid (stream 1) from spent-acid storage enters the cooling drum, where gas (stream 2) at about 170 to 180°C enters through a dip pipe below the surface of the acid and is cooled as it preheats the acid. The hot preheated

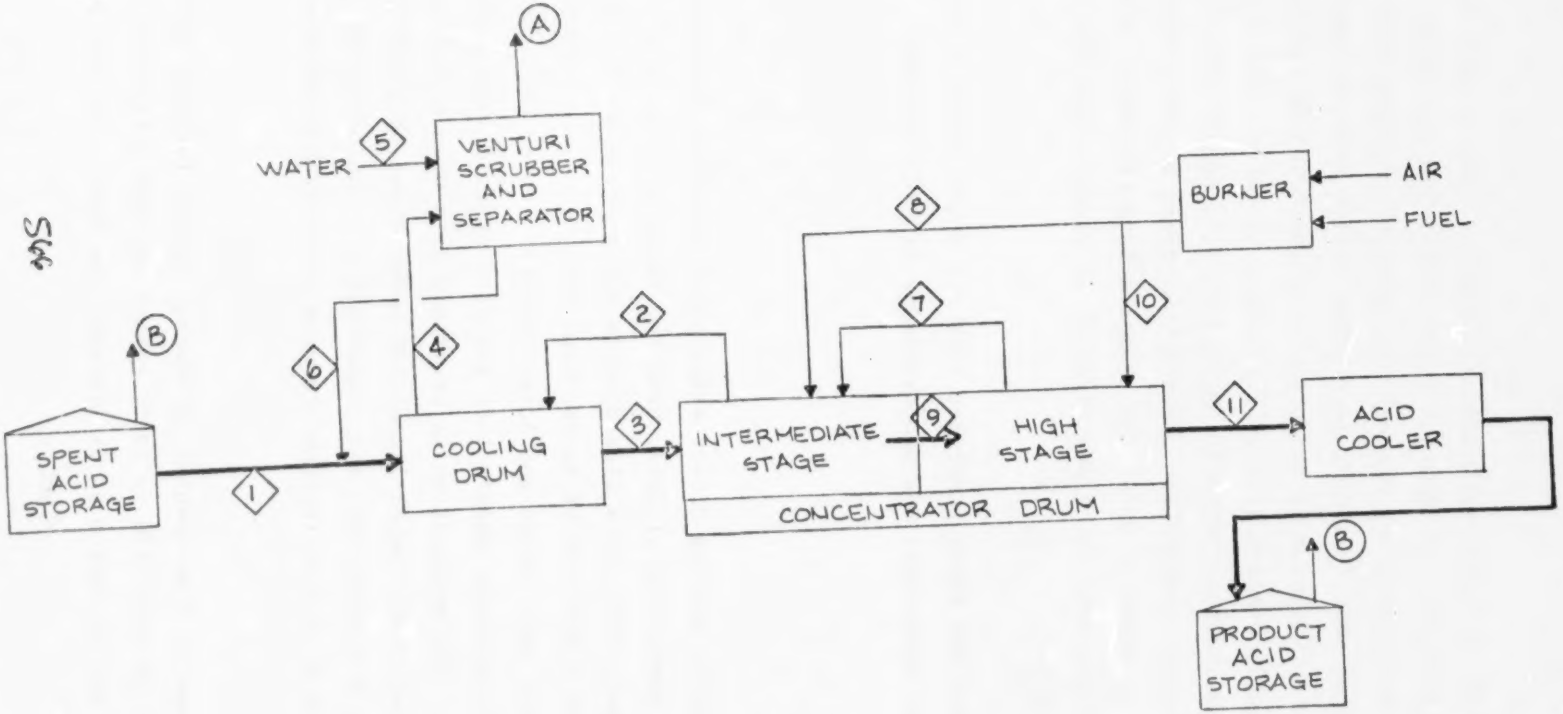
Ⓐ
WATER
5
VENTURI SCRUBBER AND SEPARATOR
Ⓑ
6
4
2
8
BURNER
AIR
FUEL
7
10
SPENT ACID STORAGE
1
COOLING DRUM
3
INTERMEDIATE STAGE
9
HIGH STAGE
CONCENTRATOR DRUM
11
ACID COOLER
Ⓑ
PRODUCT ACID STORAGE

Fig. III-1. Flow Diagram for Direct-Evaporation Sulfuric Acid Recovery Process

acid (stream 3) flows by gravity to the intermediate-stage compartment of the concentrator drum; the exaust gas (stream 4), which contains water vapor, acid mist, and VOC, is treated in the venturi scrubber and separator to remove sulfuric acid mist and is then released to the atmosphere (vent A). Water (stream 5) is added to the venturi scrubber and separator to maintain the proper concentration of scrubbing acid. The excess scrubbing acid (stream 6) is bled back to the cooling drum for recovery of the acid removed previously.

In the intermediate stage of the concentrator drum, hot gas (stream 7) from the high stage of the concentrator drum and some of the hot gas (stream 8) from the burner are introduced below the surface of the acid and by direct contact heat the acid and evaporate water and VOC from it. The acid (stream 9) flows by gravity to the high-stage compartment of the concentrator drum, and the hot gas (stream 2) containing the evaporated water vapor and VOC goes to the cooling drum. Similarly, part of the hot gas (stream 10) from the burner is introduced below the acid surface in the high-stage compartment to evaporate additional water so as to produce a concentrated (93 to 94%) acid (stream 11). The acid product flows by gravity to the acid cooler and product acid storage, while the hot gases (stream 7) containing water vapor and VOC go to the intermediate stage. Because the acid in the intermediate stage is less concentrated, more water can be evaporated into the hot gases (stream 7) that leave the high stage and that are saturated at the acid concentration existing there.[1,2]

Storage VOC emission sources (vents B) are the spent-acid storage and the product-acid storage. Since it is expected that most of the VOC will be removed in the concentrator, the product acid should contain little or no VOC and therefore the product-acid storage should emit little or no VOC emissions.

C. INDIRECT EVAPORATION

When spent acid is recovered by indirect evaporation, the heating medium, which may be steam or hot gases or some other conventional heat transfer medium, is separated from the spent acid by a heat exchange surface, as in a shell and tube heat exchanger, jacketed kettle, etc. The evaporation may be carried out under vacuum or at atmospheric pressure and may be a batch operation or a continuous operation using multiple units, depending on the spent-acid concentration, the desired concentration of the recovered acid, and the amount of spent acid to be processed.[1--4]

Figure III-2 is a flow diagram representig the Simonson-Mantius vacuum process[2] for recovering sulfuric acid from spent acid. Spent acid (stream 1) from spent-acid storage is pumped to the concentrator, where it is heated by steam to evaporate the water and the VOC. The water vapor and VOC gases containing traces of acid and inert gases (stream 2) go to a water-cooled condenser, where water and most of the VOC are condensed and the liquid (stream 3) flows to the condensate tank while the inert gases and noncondensed VOC (stream 4) are pulled through the vacuum-jet system. Condensed steam, VOC, and inert gases (stream 5) flow together as liquid and gas to the condensate tank, where the inert gases and noncondensed VOC are emitted (vent A). The recovered acid (stream 6) is cooled by the acid cooler and goes to product-acid storage.[1,2]

Storage VOC emission sources (vents B) are the spent-acid storage and product-acid storage. It is expected that most of the VOC will be removed in the concentrator; therefore the product acid will contain little or no VOC and the product- acid storage should emit little or no VOC emissions. Secondary emissions (C) can occur when wastewater containing VOC is sent to disposal.

D. REGENERATION

Recovery of sulfuric acid by regeneration involves thermal decomposition of the spent acid at high temperatures to sulfur dioxide, followed by processing of the sulfur dioxide gases, as in the contact process, to concentrated sulfuric acid or oleum. The reaction for the decomposition is

$$\underset{\text{(sulfuric acid)}}{H_2SO_4} \longrightarrow \underset{\text{(sulfur dioxide)}}{SO_2} + \underset{\text{(oxygen)}}{1/2O_2} + \underset{\text{(water)}}{H_2O}$$

The reaction is endothermic and is carried out at a temperature of 1000 to 1150°C, with the heat supplied by burning fuel. Excess air is supplied to ensure complete combustion of the fuel and any VOC.

After the water vapor is removed, the sulfur dioxide is converted to sulfur trioxide by catalytic oxidation:

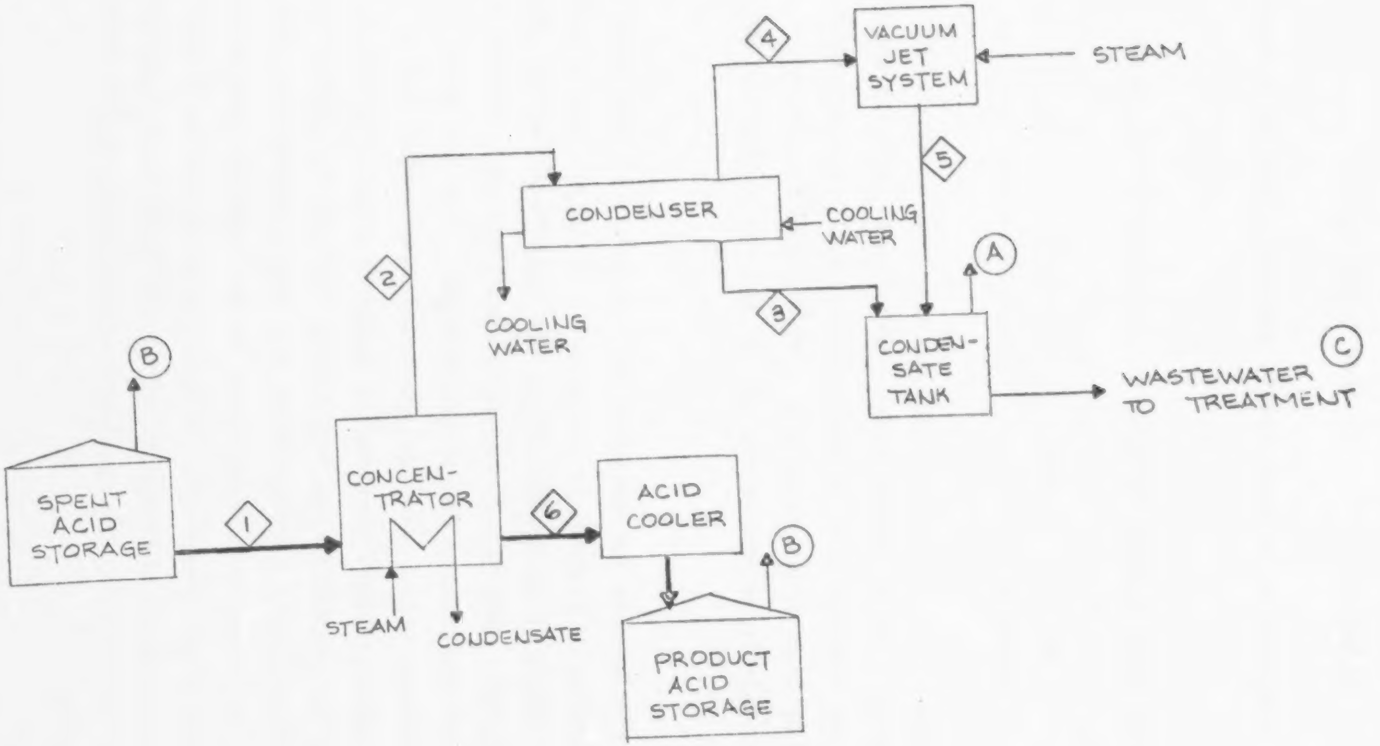
VACUUM JET SYSTEM
STEAM
4
5
CONDENSER
COOLING WATER
2
COOLING WATER
3
A
CONDENSATE TANK
C
WASTEWATER TO TREATMENT
B
SPENT ACID STORAGE
1
CONCENTRATOR
STEAM
CONDENSATE
6
ACID COOLER
B
PRODUCT ACID STORAGE

Fig. III-2. Flow Diagram for Indirect-Evaporation Sulfuric Acid Recovery Process

$$\underset{\text{(sulfur dioxide)}}{SO_2} + \underset{\text{(oxygen)}}{1/2O_2} \longrightarrow \underset{\text{(sulfur trioxide)}}{SO_3}$$

The converter inlet temperature is about 440°C and the catalyst is vanadium pentoxide.[5--8]

The sulfur trioxide is then reacted with water to form sulfuric acid:

$$\underset{\text{(sulfur trioxide)}}{SO_3} + \underset{\text{(water)}}{H_2O} \longrightarrow \underset{\text{(sulfuric acid)}}{H_2SO_4}$$

The reaction occurs when the sulfur trioxide is absorbed in strong sulfuric acid, where it combines with contained water. Both the catalytic oxidation of sulfur dioxide and the combining of sulfur trioxide and water are exothermic; the heat is removed by heat transfer to incoming streams for energy recovery or to the waste-heat boiler for steam generation or is removed by cooling water.[6--8]

Figure III-3 is a flow diagram for sulfuric acid recovery by regeneration of spent acid. The spent acid (stream 1) is pumped from spent-acid storage to the spent-acid furnace, where it is decomposed by the heat from the hot gases produced by burning fuel. Any VOC in the spent acid are also burned in the spent-acid furnace to water vapor and carbon dioxide. The hot gases (stream 2), which contain sulfur dioxide, go to the waste-heat boiler, where they are cooled by making steam. The cooled gases (stream 3) are sent to the gas cleaning system for scrubbing and for further cooling to remove water and are then sent to electrostatic precipitators for mist elimination. The cleaned gases containing sulfur dioxide (stream 4) go to the contact-type sulfuric acid plant, where they are dried, the sulfur dioxide is converted to sulfur trioxide, the sulfur trioxide is absorbed in strong sulfuric acid, and the remaining inert gases are vented (A). The sulfuric acid (stream 5) produced is sent to product-acid storage.[6,7]

The sulfuric acid plant stack (vent B) is a source of process emissions; however, no VOC are emitted because at the temperature and residence time in the spent-acid furnace all of them are destroyed.[6,7] Storage emission sources

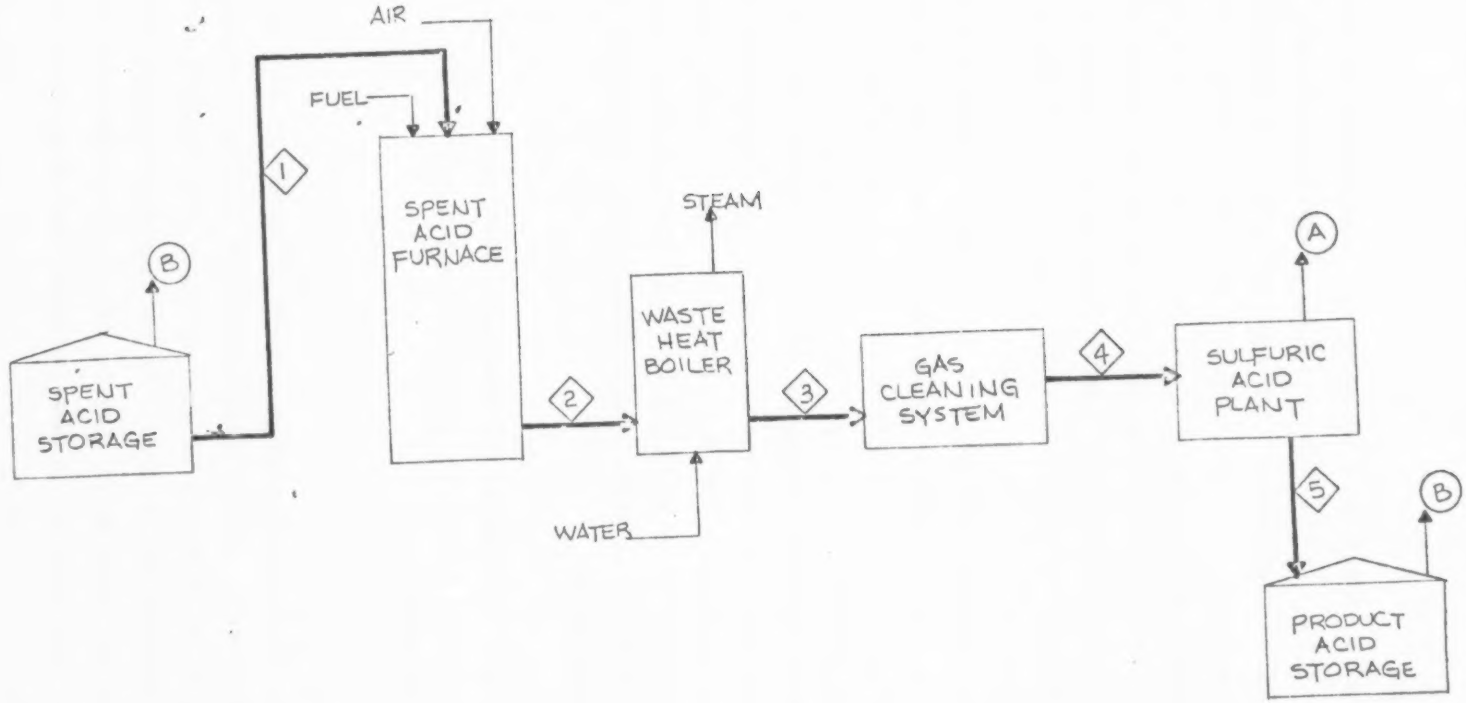
SPENT ACID STORAGE
B
1
FUEL
AIR
SPENT ACID FURNACE
2
WASTE HEAT BOILER
STEAM
WATER
3
GAS CLEANING SYSTEM
4
SULFURIC ACID PLANT
A
5
PRODUCT ACID STORAGE
B

Fig. III-3. Flow Diagram for Sulfuric Acid Recovery by Regeneration

(vent B) are the spent-acid storage and product-acid storage. Again, no VOC are emitted from product-acid storage because none are detected in the product acid.[7]

E. PROCESS VARIATIONS

The only variation in spent acid recovery is a combination of direct evaporation and regeneration. At the Rohm and Haas methyl methacrylate plant in Deer Park, Texas, a direct-evaporation technique is used to preconcentrate the spent acid before regeneration. In this process, hot gas contacts a waste acid stream to preconcentrate the acid for use as a feed to a regeneration plant. The preconcentration reduces the amount of water in the waste acid so that the acid stream can be decomposed in a regeneration plant to produce a gas with an acceptable SO_2 content for use in a contact sulfuric acid plant.[9]

The Rohm and Haas recovery technique is not currently used in any other spent-acid processing facility. Similar processes are not predicted for new plants for several reasons. First, Prevention of Significant Deterioration (PSD) regulations would prohibit new large VOC emissions without controls. The Rohm and Haas unit emits annually 500 Mg of VOC with a spent-acid capacity of around 72 Gg/yr. Control costs to conform to existing PSD regulations would be high due to volume and composition of the stack gas. Also, methyl methacrylate in the future is expected to be produced by a different process, one that does not require the use of sulfuric acid. Few companies are interested in entering the methyl methacrylate market.[9]

Since only one plant now exists and since it seems unlikely that new plants will be built for using this process, the Rohm and Haas plant is not included in the emission analysis.

F. RECOVERY TRENDS

As noted in Sect. II, an estimated 6.1 Tg/yr of sulfuric acid is processed for recovery by regeneration, direct evaporation, or indirect evaporation. Of the processes surveyed regeneration is used in about 30%, indirect evaporation in 40%, and direct evaporation in 27%. The percentage breakdown in terms of production volume is not available. Due to data limitations this division is only a rough estimate, and industry trends indicate that new plants may not have the same breakdown.

When a new plant that uses sulfuric acid is to be built, the following factors are of concern: regulatory environment, cost of control, and quality of acid required in the process. As chemical plants become part of large chemical complexes with several types of units producing spent acid, regeneration becomes more attractive. Since regeneration produces a virgin-quality acid, the acid can be used in any process that requries sulfuric acid; the use is not limited to those processes for which an impure (93%) sulfuric acid is acceptable. Direct evaporation, however, is becoming less attractive because of the regulatory environment and the cost of VOC emissions control. VOC emissions from direct-evaporation processes are several orders of magnitude higher than those from indirect evaporation. These high-flow, low-concentration emission streams are costly to control.

The trend away from direct evaporation and toward regeneration as a spent-acid recovery technique can, however, be assessed only qualitatively. This qualitative assessment of trends indicates that the worst case for emission analysis is the current industry breakdown of process utilization.

G. REFERENCES*

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2. G. M. Smith and E. Mantius, "The Concentration of Sulfuric Acid," Chemical Engineering Progress 74(9), 78—83 (1978).

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4. J. P. Walsh, Exxon Chemical Company, U.S.A., letter dated Apr. 27, 1979, containing information on air emissions from sulfuric acid recovery at Baton Rouge, LA, in response to EPA request.

5. U. Sander, "Waste Heat Recovery in Sulfuric Acid Plants," Chemical Engineering Progress 73(3), 61—64 (1977).

6. U. Sander and G. Daradimos, "Regenerating Spent Acid," Chemical Engineering Progress 74(9), 57—67 (1978).

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8. R. E. Davenport et al., "Sulfuric Acid," pp. 780.1000 A—G and 780.1001A—780.1004C in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (August 1979).

9. M. W. Karkanawi, EEA, Inc., Trip Report for Visit to Rohm and Haas, Texas, Inc., Deer Park, Texas, April 1980.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on aheading, it refers to all the text covered by that heading.

IV. EMISSIONS

The VOC emission estimates presented in this section are based on the emission data in Table IV-1.[1--17] The emission analysis is based on emission factors and sulfuric acid processing capacity derived from industry data. Emission projections are based on predicted worst-case trends in process utilization.

A. CURRENT EMISSIONS

For the plants surveyed the data on the capacity of sulfuric acid processing plants vary widely. There is little correlation between capacity and the type of recovery process used. For the purpose of emission analysis an estimated total national capacity of 6.1 Tg/yr is used, representing 190 production units.

Current VOC emission rates for the processes surveyed are shown in Table IV-1, and calculated emission factors from recovery processes are as follows:

Indirect evaporation:	30 Mg of VOC per Tg of H_2SO_4 (100%)
Direct evaporation:	1800 Mg of VOC per Tg of H_2SO_4 (100%)
Regeneration:	negligible

The emissions rate for indirect-evaporation processes was derived from the Cyanamid nitrobenzene plant, and the emissions rate for direct-evaporation processes was derived from the Allied dinitrotoluene facility (see Table IV-1). These plants were chosen for emission rate assumptions because a more complete data set is available for them.

As noted in Sect. II, an estimated 6.1 Tg of sulfuric acid is processed annually for recovery; 30% was by regeneration, 40% by indirect evaporation, and 30% by direct evaporation. Based on this industry capacity and breakdown the total nationwide VOC emission annually would be around 3.3 Gg, most of which is emitted from direct-evaporation processes. The current emissions from sulfuric acid processing then would be less than 1% of the total SOCMI VOC emissions of 680 Tg/yr. Because the estimate of sulfuric acid capacity is probably high, the current total emission estimate is also probably high.

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Table IV-1. Existing Sulfuric Acid Recovery Plant Information

Company and Location	Synthetic Organic Chemicals Produced	Sulfuric Acid Recovery Process	Spent Acid Capacity	Date Constructed	VOC Emission (Mg/yr)	Controls Used
Rohm and Haas[a]						
Deer Park, TX	Methylmethacrylate and acrylic esters	Direct evaporation and regeneration	83 Mg/hr	1970	~500	No description
Allied[b]						
Moundsville, WV	Dinitrotoluene	Direct evaporation	6.35 Mg/hr (72% spent acid)	Not reported	72	Venturi scrubber
Rubicon[c]						
Geismar, LA	(New plant) nitrobenzene	Indirect evaporation	Not reported	1979	Not reported	Organic scrubber
Dupont						
Beaumont, TX[d]	Nitrobenzene	Direct evaporation	Not reported	1972	32	Pease-Anthony venturi scrubber
Gibbstown, NJ[e]	Nitrobenzene	Direct evaporation	Not reported	Not reported	11	Not reported
Exxon[f]						
Baton Rouge, LA	Isopropyl alcohol	Indirect evaporation	93 Mg/hr (67% product acid)	Not reported	0.3	Vent condenser on one unit, returned to process from other unit
ARCO[g]						
Channelview, TX	sec-Butyl alcohol	Indirect evaporation	Not reported	Not reported	0.01	None (condenser downstream of vacuum jet not considered a control)
Shell[h]						
Deer Park, TX	sec-Butyl alcohol and isopropyl alcohol	Direct evaporation	Not reported	Not reported	Not tested	Electrostatic precipitators
Mobay						
New Martinsville, WV[i]	Nitrobenzene	Indirect evaporation	Not reported	Not reported	None reported	Thermal oxidation
Baytown, TX[j]	Dinitrotoluene	Indirect evaporation	Not reported	Not reported	None reported	Thermal oxidation
Cyanamid[k]						
Bound Brook, NJ	Nitrobenzene	Indirect evaporation	62 Mg/hr	1979	10	Organic scrubber
Dupont						
Memphis, TN[l]	Methylmethacrylate	Regeneration	Not reported	1971	None	None reported
Burnside, LA[m]	None (spent acid from off-site)	Regeneration	20 Mg/hr (spent acid - 100% basis)	1967	None	Storage emissions to sulfur burner
Stauffer[n]						
Baytown, TX	None (spent acid from off-site)	Regeneration	29 Mg/hr (84% spent acid)	Not reported	None	Storage emissions to spent-acid furnace or caustic scrubber
Allied[o]						
Richmond, CA	None (spent acid from off-site)	Regeneration	3.8 Mg/hr (spent acid - 100% basis)	Not reported	None	None reported
Olin[p]						
Beaumont, TX	None (spent acid from off-site)	Regeneration	11.5 Mg/hr (spent acid - 100% basis)	Not reported	None	Storage emissions to scrubber

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[a] See ref 1. [b] See ref 2. [c] See refs 3 and 4. [d] See ref 5. [e] See ref 6. [f] Three units are located at this site; one unit is shut down, one unit has no emissions, one unit has 0.3 Mg/yr of VOC emissions; see ref 7. [g] See ref 8. [h] See ref 9. [i] See ref 10. [j] See ref 11. [k] See ref 12. [l] See ref 13. [m] See ref 14. [n] See ref 15. [o] See ref 16.
e ref 17.

B. PROJECTED VOC EMISSIONS

It is projected that 150 new SOCMI plants will be built during the next five years.[18] Since 15% of the SOCMI plants are assumed to use sulfuric acid and process it for recovery, then 22 new plants will be sources of VOC emissions from sulfuric acid recovery in the fifth year. Also, since the current trend is toward the regeneration process and away from the direct-evaporation process, the worst case that can be reasonably projected for new sources is industry-wide additional VOC emissions of 2.5 Gg/yr. This is based on the current estimated process breakdown of 30% by regeneration, 40% by indirect evaporation, and 30% by direct evaporation and on 4.7 Tg/yr of additional sulfuric acid processing capacity in the fifth year. This is a worst-case estimate, and VOC emissions will probably be less.

C. SULFUR DIOXIDE (SO_2) AND H_2SO_4 MIST EMISSIONS

The standards of performance for new contact-process sulfuric acid facilities for SO_2 and acid mist apply to the regeneration process used for spent-acid recovery. They do not apply to the direct- and indirect-evaporation methods of acid concentration. The emission limitations required that no more than 2.0 kg of SO_2 per metric ton of acid (100% H_2SO_4) be emitted and that no more than 0.75 kg of acid mist per metric ton of acid (100% H_2SO_4) produced be emitted.[19]

Table IV-2 summarizes the SO_2 emissions and H_2SO_4 mist emissions from the three types of recovery methods. Some SO_2 will often be formed in the evaporation processes by the reduction of H_2SO_4 by organic components in the stream. The SO_2 emissions are small; no SO_2 is usually detected from indirect processes and only small amounts from direct processes.

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Table IV-2. Emissions from Sulfuric Acid

Recovery Process	Emission Ratio (g/kg)[a]		
	VOC	Sulfur Dioxide	Sulfuric Acid Mist
Regneration	Negligible	2.0[b]	0.075[b]
Direct Evaporation[c]	1.8	0.2	0.3
Indirect evaporation[d]	0.033	None detected	None detected

[a] g of emission per kg of sulfuric acid (100% basis) produced.

[b] Based on NSRS emission limits for sulfuric acid plants.

[c] See ref 2.

[d] See ref 12.

D. REFERENCES*

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6. R. C. Ott, Dupont, letter dated May 26, 1978, containing information on air emissions from nitrobenzene process at Gibbstown, NJ, in response to EPA request.
7. J. P. Walsh, Exxon Chemical Co., U.S.A., letter dated Apr. 27, 1979, containing information on air emissions from sulfuric acid concentrators at Baton Rouge, LA, in response to EPA request.
8. C. N. Hudson, Arco Chemical Co., letter dated Apr. 30, 1979, containing information on air emissions from sulfuric acid concentrators at Channelview, TX, in response to EPA request.
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15. J. W. Call, Stauffer Chemical Co., letter dated Aug. 6, 1979, containing information on air emissions from spent-acid recovery process at Baytown, TX, in response to EPA request.

16. W. M. Reiter, Allied Chemical, letter dated May 8, 1979, containing information on air emissions from spent-acid recovery process at Richmond, CA, in response to EPA request.

17. H. T. Emerson, Olin Corp., letter dated May 14, 1979, containing information on air emissions from spent-acid recovery process at Beaumont, TX, in response to EPA request.

18. E. Hurley, EEA, Inc., personal communication with B. Newman, EEA, Inc., August 1980.

19. Background Information for Proposed New Source Performance Standards for Sulfuric Acid Plants, EPA, APTD-0711 (August 1971).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. DIRECT EVAPORATION

The venturi scrubber and separator shown on Fig. III-1 for the direct-evaporation sulfuric acid recovery process is an emission control device primarily intended to remove acid mist from the vent gases (A, Fig. III-1) before they are released to the atmosphere.[1] Some VOC may be removed by these devices if they are soluble in the scrubbing medium or if they are in particulate form. No measured removal-efficiency data were reported, although one respondent estimated that the venturi scrubber would remove 60% of the nitroaromatics from the vent gases.[2] However, it is believed that the VOC removal efficiency of most of the reported control devices is very low. No add-on control device has been identified that will significantly reduce the reported VOC emissions from the direct-evaporation plants shown in Table IV-1.

One technique for emission control that was reported is the replacement of a plant that used direct-evaporation sulfuric acid recovery with a new plant, one which uses indirect evaporation. Two companies have started up new nitrobenzene plants that employ new technology, including an indirect-evaporation sulfuric acid recovery process.[3] Data are not available on VOC emissions from the new plants, but it is believed that there will be a net reduction if the old direct-evaporation plants are shut down.

A possible control technique that has not been reported or investigated is source control, which results in reduction of the more soluble VOC in the spent acid going to the direct-evaporation process. If the VOC can be removed completely from the spent acid, then, of course, there should be no VOC emissions from a direct-evaporation sulfuric acid recovery process.

B. INDIRECT EVAPORATION

The VOC emissons from the condensate tank (vent A, Fig. III-2) in an indirect-evaporation sulfuric acid recovery process may be controlled by thermal oxidation, by return to the process where the spent acid was produced, or by condensation in a vent condenser (see Table IV-1). A thermal oxidizer with adequate residence time and temperature will destroy 98% or greater of the VOC emissions. Separate EPA reports cover the evaluation of emission control devices

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and the conditions affecting their efficiency. The return of emissions to the process reportedly[4] results in 100% reduction of emissions but the reduction efficiency of the vent condenser was not reported.

C. REGENERATION

As no VOC are emitted with the vent gases (A, Fig. III-3) from a sulfuric acid recovery by regeneration process, no control devices are needed.

D. STORAGE

VOC emissions from the spent-acid storage (B, Fig. III-3) may be controlled by thermal oxidation. The vent on the spent-acid storage tank is connected to the sulfur burner air intake at one sulfuric acid plant so that a portion of the air required by the burner comes from the vapor space of the spent-acid tank.[5] Another plant controls the VOC emissions from the spent-acid storage by feeding them to the spent-acid furnace.[6] No data are available on the reduction efficiency at these plants; however, no VOC are reported in the vent gases.[5,6]

E. REFERENCES*

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3. "Chementator," Chemical Engineering 86(14), 27 (1979).

4. J. P. Walsh, Exxon Chemical Co., U.S.A., letter dated Apr. 27, 1979, containing information on air emissions from sulfuric acid concentrators at Baton Rouge, LA, in response to EPA request.

5. J. A. Key, IT Enviroscience, Trip Report for Visit to E. I. du Pont de Nemours & Company, Inc., Burnside, LA, Apr. 24, 1979 (on file at EPA, ESED, Research Triangle Park, NC).

6. J. W. Call, Stauffer Chemical Co., letter dated Aug. 6, 1979, containing information on air emissions from spent-acid recovery process at Baytown, TX, in response to EPA request.

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VI. IMPACT ANALYSIS

Environmental, energy, and control cost impacts have not been determined for the control devices discussed in Sect. V.

Appendix A

EXISTING PLANT CONSIDERATIONS

The controls discussed in Sect. V may not be applicable to existing plants. No effective add-on control has been identified for the large volume of gases containing VOC that are vented from a direct-evaporation sulfuric acid recovery process. Retrofit of a thermal oxidizer to control the VOC from an existing indirect-evaporation sulfuric acid recovery process can be very costly because of space limitations, production lost during installation and startup, etc., and be appreciably greater than for a new installation. Replacement of an existing direct-evaporation sulfuric acid recovery process with an indirect-evaporation process may not be feasible for the same reasons. The existing direct-evaporation processes are in older plants, which were built before VOC emissions were of concern. For example, the Rohm and Haas plant processes spent acid from several organic chemical production units where spent-acid strippers are used to recover organic values before the spent acid goes to the combined direct-evaporation and regeneration sulfuric acid recovery plant. The feed rate to the direct- evaporation concentrators is controlled to limit emissions of VOC to 250 lb/hr per concentrator as required by the Texas Air Control Board rules. The acid from the direct-evaporation concentrators is then recovered in a regeneration process that produces 99% sulfuric acid. To change from direct evaporation to indirect evaporation would require installation of new indirect-evaporation concentrators and probably demolition of the existing concentrators, resulting in considerable lost production and expense. Available data are not adequate for an estimate to be made of this cost.